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# ***JPRS Report—***

## **Science & Technology**

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***Central Eurasia:  
Chemistry***

# Science & Technology CENTRAL EURASIA: Chemistry

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**State of Cu Ions in Catalysts Promoting Oxidation of CO to CO<sub>2</sub>**

927M0187A Moscow *IZVESTIYA ROSSIYSKOY AKADEMII NAUK: SERIYA KHMICHESKAYA* in Russian No 4, Apr 92 (manuscript received 09 Aug 91) pp 786-790

[Article by M.A. Ismailov, R.B. Akhverdiyev, V.S. Gadzhi-Kasumov, V.I. Yakerson and V.G. Sarmurzina, Institute of Organic Chemistry imeni N.D. Zelinskiy, Russian Academy of Sciences, Moscow; UDC 541.128]

[Abstract] Electron diffusion reflection (EDR) spectroscopy was used to analyze the states of Cu atoms in two classes of metallic catalysts used for oxygenation of CO to CO<sub>2</sub>. Group A catalysts were prepared by fusing activated metallic Al (containing 3% In and 3% Ga) with 1-40% by wt. of Cu and calcining at 300-700°. Group B catalysts were synthesized by impregnation of metallic Al that had been roasted at 500° with Cu(NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O (Cu = 1-40% by wt.), followed by calcining. In both cases increasing the Cu concentration decreased the temperature for maximum oxygenation. Best results—maximum catalytic activity at 220°—were obtained with A catalysts containing 10% Cu and B catalysts containing 40%. EDR spectra correlated high catalytic activity with saturation of catalyst surface with free CuO and reduction of the concentration of Cu<sup>++</sup>(O<sub>h</sub>) ions. Accordingly, A catalysts appear to be more suitable as a relatively inexpensive alternative to the more expensive platinum-group catalysts for oxygenation of CO to CO<sub>2</sub>. Figures 4; references 7: 5 Russian, 2 Western.

**Cyclohexene Hydrogenation on Various Catalysts**

927M0187B Moscow *IZVESTIYA ROSSIYSKOY AKADEMII NAUK: SERIYA KHMICHESKAYA* in Russian No 4, Apr 92 (manuscript received 24 Apr 91) pp 791-799

[Article by V.V. Kharlamov, V.I. Garanin (dec), S.N. Karakhotin and Kh.M. Minachev, Institute of Organic Chemistry imeni N.D. Zelinskiy, Russian Academy of Sciences, Moscow; UDC 542.97:547.313:661.183.6]

[Abstract] A comparative assessment was made of the energies of activation (E<sub>a</sub>) for isomerization of the cyclohexyl skeleton during hydrogenation of cyclohexene on zeolite, metal oxides and palladium catalysts. Arrhenius plots yielded E<sub>a</sub> values of 83-96 kJ/mole for Na- and K-forms of zeolites and erionite [sic], 33-50 kJ/mole on H-types of zeolites, 33-37 kJ/mole on Pd/SiO<sub>2</sub> and Pd/a-Al<sub>2</sub>O<sub>3</sub> catalysts, and 25-33 kJ/mole on MgO, and La<sub>2</sub>O<sub>3</sub>. In conjunction with the products formed in the flow-through reactor (cyclohexane, methylcyclopentane, methylcyclopentene isomers), the data indicated that on Na-zeolites hydrogenation proceeds via an intermediate carbanion. Figures 3; tables 3; references 32: 18 Russian, 14 Western.

**Electrochemical and Chemical Oxidation of Alcohols in Utilizing N-Oxypiperidinium Salt: Synthesis of 4-Chlorobutanal, Formylcyclopropanes and m-Phenoxybenzaldehyde**

927M0187D Moscow *IZVESTIYA ROSSIYSKOY AKADEMII NAUK: SERIYA KHMICHESKAYA* in Russian No 4, Apr 92 (manuscript received 9 Apr 91) pp 941-945

[Article by Yu.N. Ogibin, A.Kh. Khusid and G.I. Nikishin, Institute of Organic Chemistry imeni N.D. Zelinskiy, Russian Academy of Sciences, Moscow; UDC 541.138.1:542.943:547.446:547.512:547.571]

[Abstract] 2,2,6,6-Tetramethyl-4-benzyloxy piperidine-1-oxyl (TMBP)(tab) was employed in conjunction with electrochemically generated bromine ions, molecular bromine and sodium hypochlorite for oxidative dehydrogenation of alcohols. Trials on oxidation of 4-chlorobutanol-1, cyclopropylcarbinols, and m-phenoxybenzyl alcohol were conducted at ca. 20° C in 5% NaHCO<sub>3</sub> + 20% NaCl in aq. CH<sub>2</sub>Cl<sub>2</sub> or 5% NaHCO<sub>3</sub> + NaBr and 1-2 mole% TMBP, pH 8.6, with the application of a 2-2.7 F current. This approach resulted in the conversion of the alcohols to 4-chlorobutanal, formylcyclopropanes, and m-phenoxybenzaldehyde, respectively, in 60-70% yields. Tables 1; references 22: 6 Russian, 16 Western.

**Catalytic Synthesis and Transformations of Magnesium Cycloalkanes. Part 2. Zirconium Complex-Catalyzed Synthesis of Magnesium Cyclopentanes**

927M0187E Moscow *IZVESTIYA ROSSIYSKOY AKADEMII NAUK: SERIYA KHMICHESKAYA* in Russian No 4, Apr 92 (manuscript received 04 Feb 91) pp 980-998

[Article by U.M. Dzhemilov, R.M. Sultanov, R.G. Gaymaldinov, R.R. Muslukhov, S.I. Lomakina and G.A. Tolstikov, Institute of Organic Chemistry, Urals Department, Russian Academy of Sciences, Ufa; UDC 542.97:542.91:547.254.6]

[Abstract] Studies were performed on one-stage cyclometallation of styrene, m-methy- and p-tert-butylstyrenes and 1-hexene by n-R<sub>2</sub>Mg alkyls (R = C<sub>3</sub>H<sub>7</sub>, C<sub>4</sub>H<sub>9</sub> or C<sub>6</sub>H<sub>13</sub>) on a Cp<sub>22</sub>ZrCl<sub>2</sub> catalyst. The method was shown to be efficient for synthesis of 2,4-substituted magnesium cyclopentanes in 70-85% yields. A probable scheme has been proposed for the reaction, involving the formation of intermediate α-, β'-bisubstituted Zr-cyclopentanes that undergo transmetallation to the Mg-cyclopentanes and regeneration of the Zr catalyst. Tables 3; references 9: 6 Russian, 3 Western.

**CO Removal by Adsorption on Catalytic Surfaces**

927M0238A Moscow ZHURNAL PRIKLADNOY KHIMII in Russian Vol 65 No 2, Feb 92 (manuscript received 19 Dec 91) pp 269-274

[Article by V.M. Vlasenko, S.A. Solovyeva and G.M. Belokleytseva, Institute of Physical Chemistry imeni L.V. Pisarzhevskiy, Ukrainian Academy of Sciences; UDC 541.1+661.183:546.262]

[Abstract] Adsorption of CO to catalytic surfaces was found to be an efficient method for its removal from gas mixtures without significantly raising the temperature of the gas. The most suitable class of catalysts was identified as 16-18% MnO<sub>2</sub> on 82-84% mordenite carrier (MKP-1 catalysts). These catalysts exhibit high adsorptive areas ( $8.6 \text{ cm}^2 \text{ gm}^{-1}$ ), retain activity for 94-95 min, and limit the temperature rise to 1.6-1.9 K. Furthermore, they are fully regenerated by heating at 608-613 K. Highest activities were displayed by catalysts in which mordenite was impregnated with MnO<sub>2</sub> at pH 6, a procedure that favors the appearance of the MnOOH phase in MnO<sub>2</sub>. Figures 2; tables 2; references 11: 10 Russian, 1 Western.

**Partial Oxidation of Methanol to Formaldehyde on Ag Catalysts**

927M0238B Moscow ZHURNAL PRIKLADNOY KHIMII in Russian Vol 65 No 2, Feb 92 (manuscript received 20 Dec 90) pp 275-278

[Article by A.N. Devochkin, A.N. Pestryakov, L.N. Kurina and A.A. Sakharov, Tomsk State University; UDC 541.128:661.721]

[Abstract] Comparative analysis was conducted on several types of Ag catalysts for oxidation of methanol to formaldehyde in an effort to improve this important commercial process. The trials encompassed carrier-based (Ag/pumice, LNKh-M) and solid (crystalline Ag, SD, SK) catalysts, and resulted in tabulated data on process temperatures, O<sub>2</sub>:CH<sub>3</sub>OH ratios, formaldehyde yields, rates of conversion, and selectivity. The resultant data demonstrated the advantages and disadvantages of the different types of Ag catalysts, and the feasibility of securing good yields with low-Ag SD and SK catalysts. Tables 1; references 5: Russian.

**Catalytic Pyrolysis in Synthesis of Carbon-Containing Adsorbents**

927M0238G Moscow ZHURNAL PRIKLADNOY KHIMII in Russian Vol 65 No 2, Feb 92 (manuscript received 15 July 91) pp 457-459

[Article by A.A. Dits and V.N. Potnov, St. Petersburg State University; UDC 541.183]

[Abstract] Novel adsorbents were prepared by treating an aerosilicagel carrier with titanium tetrachloride vapors, molecular overlaying with methyl methacrylate,

and pyroprocessing at 600° under an inert gas in a flow reactor. Increasing the titanium concentration was shown to lead to a symbiotic increase in the carbon content. After 4 processing cycles the final adsorbent showed heats of adsorption of 66.7, 64.5 and 77.1 kJ/mole for p-hexane, benzene and toluene, respectively. Accordingly, such adsorbents may have extensive analytical and ecological applications vis-a-vis organics. Tables 2; references 8: 1 Polish, 6 Russian, 1 Western.

**Synthesis of Pyridine Bases From Dimethylethynylcarbinol, Acetaldehyde and Monoethanolamine on Heterogenous Catalyst**

927M0238H Moscow ZHURNAL PRIKLADNOY KHIMII in Russian Vol 65 No 2, Feb 92 (manuscript received 14 Mar 91) pp 465-467

[Article by A. Ikramov, T.S. Sirlibayev and M.F. Faizulayeva, Tashkent State University imeni V.I. Lenin; UDC 547(821.362.281.233):546.171.1]

[Abstract] Two approaches were evaluated for the synthesis of pyridine bases via catalytic condensation on a AlF<sub>3</sub>(7%)/ZnO(3%)/Cr<sub>2</sub>O<sub>3</sub>(87%) catalyst at 300-420° C. Condensation of dimethylethynylcarbinol (DMEC) with acetaldehyde and ammonia (1:1:3) and of DMEC with monoethanolamine (1:1) yielded identical products, consisting of 2- and 4-methylpyridine, 2,4-dimethylpyridine, 2,4,6-trimethylpyridine, acetonitrile and higher pyridine bases. In both cases product proportions were temperature-dependent. Tables 1; references 12: 11 Russian, 1 Western.

**A Study of the Catalytic Activity of Mono- and Polynuclear Iron-Containing Systems in the Hydrogenation of Brown Coal Combined With Bituminous Oil**

937M0047A Moscow KHIMIYA TVERDOGO TOPLIVA in Russian No 3, May-Jun 92 (manuscript received 18 Jun 91) pp 46-54

[Article by M.V. Tsodikov, Yu.V. Maksimov, G.A. Teplyakova, O.V. Bukhtenko, M.M. Grozhan, M.A. Perederiy, and S.M. Loktev, Petrochemical Synthesis Institute, Russian Academy of Sciences; UDC 662.743-552.576]

[Abstract] A study examined the interconnection of the structure of applied iron-containing complexes and their catalytic activity during the process of the hydrogenation of the organic matter of brown coal in a Tetralin medium, as well as in a medium of sulfur donor, i.e., bituminous oil containing more than 4 wt.-% S. Pulverized, predried brown coal from the Irsha-Borodinskoye deposit of the Kansk-Achinsk Basin was used as a raw material. Freshly distilled Tetralin and bituminous oil isolated from the sands of the Ashalchinskoye bitumen deposit was used as paste-forming agent. Mono- and heteronuclear acetylacetones of transition metals were used to prepare the catalysts. The hydrogenation was

conducted in a 0.5-l-capacity autoclave with a stirring device at a hydrogen pressure of 10 MPa. X-ray diffraction and Mossbauer spectroscopy studies performed on the specimens established that the application of heteronuclear iron-cobalt and iron-molybdenum acetylacetone complexes to the surface of brown coal before hydrogenation results in a nonadditive increase in the conversion of the organic matter of the coal-oil paste when compared with when the same coal is coated with mononuclear complexes prior to hydrogenation. The studies also established that the catalytic activity observed is the result of the formation of heteronuclear nonstoichiometric compounds of the type  $Fe_xM_{1-x}S_y$  ( $M =$  cobalt or molybdenum) on the coal's surface. It was hypothesized that defects in the sulfided heteronuclear transition metal clusters are catalytic centers of the decomposition of sulfur-containing organic compounds that in turn result in high indicators with respect to the desulfurization of bituminous oil during the process of its combined processing with coal. Figures 4, tables 3; references 9: 6 Russian, 3 Western.

#### Using Coals as Carriers of Heterogeneous Catalysts of the Carbonylation of Nitrobenzene

937M0047B Moscow KHIMIYA TVERDOGO TOPLIVA in Russian No 3, May-Jun 92 (manuscript received 9 Oct 91) pp 55-59

[Article by A.R. Tumanova, S.D. Pirozhkov, and A.L. Lapidus, Organic Chemistry Institute, Russian Academy of Sciences; UDC 541.128:542.92:547.21]

[Abstract] The synthesis of ethyl-N-phenylcarbamate by carbonylation of nitrobenzene in an ethanol medium with a palladium-on-coal catalyst was examined in a systematic study. Eleven different Pd/C catalysts were studied. In some cases the palladium was applied to the coal by adsorption; in other cases it was applied by the technique of spraying based on moisture capacity. The carbonylation was conducted in a rotary autoclave (capacity, 0.5 l) made of Cr18Ni10Ti steel with a glass insert. The following were used in each experiment: 5 cm<sup>3</sup> C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>, 0.6 cm<sup>3</sup> Py, and 15 cm<sup>3</sup> C<sub>2</sub>H<sub>5</sub>OH. A CHROM-5 chromatograph was used to perform gas-liquid chromatography studies on the reaction products. All of the catalysts studied proved to be active in the synthesis of ethyl-N-phenylcarbamate. The degree of palladium oxidation did not have any marked effect on the process. Specimens reduced by different compounds at different temperatures were found to display varying degrees of activity. These differences were attributed to differences in the dispersion of the metal. It was demonstrated that contacts containing subunit-type coal as a carrier are most active in the ethyl-N-phenylcarbamate synthesis process. None of the catalysts tested had a high stability: After three or four successive experiments, nitrobenzene conversion and, more importantly, ethyl-N-phenylcarbamate yield decreased. Figures 2, tables 4; references 4 (Russian).

#### Catalytic Scrubbing of Nitrogen Oxides and Sulfur Dioxide From Stack Gases. 2. Scrubbing Sulfur Dioxide From Gases

937M0049A Alma-Ata IZVESTIYA AKADEMII NAUK KAZAKHSKOY SSR: SERIYA KHIMICHESKAYA in Russian No 2, Mar-Apr 92 (manuscript received 10 Jun 91) pp 9-13

[Article by K.A. Zhubanov, N.R. Bukeykhanov, V.S. Yemelyanova, K.R. Shayakhmetova, S.A. Tungatarov, and T.S. Khairliyeva, Petrochemistry and Chemistry of Natural Salts Institute, Republic of Kazakhstan Academy of Sciences, Guryev; UDC 546:172.541.943]

[Abstract] Because of the biphasic nature of sulfur dioxide, catalytic methods of scrubbing it from stack gases involve the oxidation of SO<sub>2</sub> to SO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> or reduction to sulfur. Platinum is the most active catalyst of the oxidation of SO<sub>2</sub>. Among oxides, V<sub>2</sub>O<sub>5</sub> manifests the highest activity as a sulfur dioxide-oxidizing catalyst at 400° C; at 550° C, it is four orders of magnitude less active than platinum, however. Sulfates of alkaline and alkaline earth metals are used as V<sub>2</sub>O<sub>5</sub> promoters. Studies of the oxidation of aqueous solutions of sodium sulfate in the presence of different catalysts have established that the reaction rate increases in proportion to increases in the concentration of SO<sub>3</sub><sup>2-</sup> in the solution and is, for practical purposes, independent of the partial pressure of oxygen in the gas. Sulfur-scrubbing methods involving the reduction of SO<sub>2</sub> to sulfur are considered more economical. Several developments in this field have reached the commercial test stage. The process is based on the reduction of an aqueous solution of sodium sulfate by sodium sulfide to result in sulfur and sulfate. In the former Soviet Union work has recently been done in the direction of the catalytic scrubbing of SO<sub>2</sub> from gases based on a liquid-phase Claus reaction in a medium of triisobutylphosphate in the presence of a diocetylaminopropionitrile catalyst. Laboratory and pilot tests have established the high activity and stability of the catalyst and the virtually total removal of SO<sub>2</sub> from the gas. A search of patent applications submitted in the FRG and former USSR has revealed that sulfur dioxide may be reduced by coal and carbon oxide. Further literature searches have established that the problem of scrubbing nitrogen oxides and sulfur dioxide from stack gases is receiving increasing attention in the industrially developed countries and will likely receive even more attention as environmental protection regulations become increasingly more stringent. In the former USSR stack gases are currently only being cleansed of their ash with an average efficiency of 94.2%. Four methods of scrubbing sulfur dioxide from stack gases are currently in the assimilation stage: 1) the magnesite-cyclic method; 2) the ammonia-ozone method; 3) the cyclic ammonia method; and 4) the wet lime method. The development and commercial assimilation of catalysts for selective reduction of nitrogen oxides by ammonia is still in the development stage. Ammonia catalyst systems for decomposing nitrogen oxides with an efficiency of 85% are already prevalent abroad. The capital investments

for the equipment amount to about 50 rubles/kW. Commercial assimilation of the process in the former USSR is slated for 1992-1994. Table 1; references 17: 8 Russian, 9 Western.

### The Catalytic Activity of Metal Sulfides and Oxides During the Hydrogenation of Coals by Carbon Oxide and Water. Part 1

*937M0049E Alma-Ata IZVESTIYA AKADEMII NAUK KAZAKHSKOY SSR: SERIYA KHIMICHESKAYA in Russian No 2, Mar-Apr 92 (manuscript received 14 Feb 91) pp 74-78*

[Article by B.T. Yermagambetov, V.A. Khrupov, A.Ya. Chen, M.I. Baykenov, A.L. Lapidus, and S.D. Pirozhkov, Organic Synthesis and Coal Chemistry Institute, Republic of Kazakhstan Academy of Sciences, Karaganda; UDC 662.743.552.578]

[Abstract] A series of studies were conducted to determine the effect of a number of metal sulfides and oxides on the degree of transformation of different types of coals in different hydrogenation media. Samples of coal from four different deposits were subjected to hydrogenation in a rotary autoclave (capacity, 0.5 l) at a temperature of 698 K as follows: 1.5 g wet coal and 30 g "commercial-grade" Tetralin, 1.5 g catalyst, and 18 g water were placed in the autoclave and blasted with carbon oxide to remove the air. A gauge CO pressure of 4 MPa was established, and the autoclave was heated at a rate of 15° C/min. The experiment was considered to have started the moment the specified temperature was reached. Each experiment lasted 90 minutes. After the autoclave had been cooled, the liquid products were separated from the solid residue. The solid products were extracted with an alcohol-benzene solvent for 24 hours. After the solid residue had been dried at 378 K, it was analyzed to determine its carbon, hydrogen, ash, and moisture contents. The liquid coal destructive hydrogenation products were separated into three fractions: oils, asphaltenes, and preasphaltenes. Gas-liquid chromatography studies were performed on a CHROM-5 to analyze the composition of the gaseous phase. Ferrochrome, pyrrhotine concentrate, pyrite concentrate, iron oxide, and molybdenum concentrate were used as catalysts. In a CO/H<sub>2</sub>O medium, the greatest yield (81.11%) was obtained when pyrite was used as the catalyst. The lowest yield (56.63%) was observed when the pyrrhotine concentrate was used. Of the coals studied, those from the Irsha-Borodinskoye deposit were most easily hydrogenated (they contained the highest amounts of oils and the lowest amount of asphaltenes). The coals of the Donets Basin were not as easily subjected to destructive hydrogenation; their liquid products only contained 10.46% asphaltenes. Analysis of the gaseous-phase products revealed that the degree of hydrogenation depends on the amount of hydrogen evolved when the carbon oxide

is converted, and the petrographic and mineralogic compositions of the starting coal are decisive in carbon oxide conversion. The degree of hydrogenation was thus found to depend not just on the catalyst used but also on the process temperature and the structure and degree of carbonization of the organic mass of the coal. Tables 4; references 7: 2 Russian, 5 Western.

### Coal-Containing Porous Composites for Adsorption and Catalysis

*937M0051A Moscow KHIMICHESKAYA PROMYSHLENNOST in Russian No 2, Feb 92 pp 76-78*

[Article by N.A. Prokudina, R.A. Buyanov, and V.V. Chesnokov; UDC 66.097.5.002.237]

[Abstract] Mineral-based carbon-containing composites combine the virtues of mineral sorbents and activated charcoals. Specifically, they feature a high level of mechanical strength and hydrophobicity. A study was conducted to develop carbon-containing composites based on γ-Al<sub>2</sub>O<sub>3</sub> that could be used in adsorption and catalysis processes. Five different C-Al<sub>2</sub>O<sub>3</sub> composites were developed: two C-Al<sub>2</sub>O<sub>3</sub> composites with 12 and 19% carbon, respectively; two C-Ni-Al<sub>2</sub>O<sub>3</sub> composites that contained 29 and 38% carbon, respectively; and a C-Fe-Al<sub>2</sub>O<sub>3</sub> composite that contained 40% carbon. The composites were used as carriers for a mercuric chloride catalyst for synthesizing vinylchloride by vapor-phase hydrochlorinated acetylene and for use in gas chromatographic separation of C<sub>1</sub>-C<sub>4</sub> saturated and unsaturated hydrocarbons. The mineral carrier's surface was "encased" in a carbon film that changed only the chemical composition of the surface and left the specific surface unchanged. A way was then found to give the new composites unique properties by carbonizing the metal catalysts based on a carbide cycle. Specifically, the surface of the mineral base was modified with fine-crystal metal particles (Fe and Ni) on which hollow graphite threads measuring 5 nm or more in diameter then grew. These threads filled the inner pore spaces of the mineral sorbent, thus increasing the total surface of the composite from 200 to 400 m<sup>2</sup>/g. The composite sorbents were then treated with mineral acid solutions. This resulted in the formation of a large number of pores (as a result of the dissolution of the metal particles at the ends of the carbon threads) and opened access to the total inner channel of threads. This resulted in an increase in the composite sorbents' specific surface (by about 100 m<sup>2</sup>/g), pore size (by 0.10 to 0.15 cm<sup>3</sup>/g), and adsorbency. The modified carbon-containing porous composites have adsorption characteristics approaching those of activated charcoals but are superior to the activated charcoals from a mechanical strength standpoint. The new carbon-containing composites may be produced by decomposing hydrocarbons on inorganic carriers in a cyclic mode with hydrogen as a by-product. Figures 2, tables 2; references 17 (Russian).

**The Change in the Composition of a Depleted Vanadium Sulfuric Acid Catalyst by Depth of the Layer in the Contact Device**

937M0051C Moscow KHIMICHESKAYA  
*PROMYSHLENNOST* in Russian No 2, Feb 92  
pp 92-96

[Article by P.M. Zaytsev, V.N. Talanov, and I.S. Smirnova; UDC 661.25:66.097.322]

[Abstract] The amounts of sulfur dioxide oxidized in the different layers of a vanadium catalyst in a contact device operating in a single- or double-contact mode differ from one another owing to differences in the temperature conditions existing in each layer. In a 1-m layer, for example, the gas at the entry has a temperature of 435-440° C while the gas at the exit has a temperature of 590-600° C. The gas then enters the second layer at a temperature of 448-452° C and exists at a temperature of 510-520° C. In 3-m, 4-m, and 5-m layers the temperature differences are not as great (about 20, 15, and 2° C, respectively), with the temperature of the incoming gas ranging from 430-440 in 3-m and 4-m layers up to 420-425° C in a 5-m layer. The main components of the contact gas stream may have one or two unshared pairs of electrons and also differ from one another with respect to stereochemical structure. Vanadium sulfuric acid catalysts are known to be subject to such temperature differences. A study was therefore conducted to examine the change in composition of a vanadium catalyst throughout the depth of single- or double-layer contact devices when the temperatures of the gas stream at the entry and exit of the layers amounts to about 160 and 70°, respectively. Freshly prepared and depleted (after 10 months of use) vanadium catalysts were examined. A VRA-30 x-ray spectrometer was used to determine the change in the composition of the depleted catalyst in the first layer of a contact device with a precision of +/-2.0 to 3.2% (rel.). The composition of the depleted catalyst throughout the depth of its layer was found to depend on the nature of the carrier. Marked changes in composition occurred when silica gel carriers were used. When diatomite and belax were used as carriers, the catalyst's composition remained virtually unchanged throughout the depth of the catalyst layer. The quantitative changes in the composition of vanadium catalysts throughout their depth in single- and double-layer sulfuric acid contact devices operating on the basis of elemental sulfur were attributed to the transfer of SiO<sub>2</sub> from the upper part of the layer to the lower part. This transfer of SiO<sub>2</sub> was in turn attributed to the formation of volatile oxygen-containing silicic acids at low temperatures (430-480° C) in the upper parts of the contact layers followed by their dehydration at higher temperatures (500-600° C) in the lower parts of the contact layers. It was concluded that the operating life of vanadium catalysts could be extended by using a diatomite (which is less subject to the aforementioned effect) as a base. Figure 1, tables 3; references 15: 12 Russian, 3 Western.

**The Optimal Distribution of Catalyst in Double- and Triple-Contacting Sulfuric Acid Systems**

937M0051D Moscow KHIMICHESKAYA  
*PROMYSHLENNOST* in Russian No 2, Feb 92  
pp 105-107

[Article by S.V. Ivanenko; UDC 661.248:541.127]

[Abstract] Several dozen equations have been proposed to describe the process of the oxidation of SO<sub>2</sub> on vanadium catalysts; however, each is only suitable in comparatively narrow ranges of temperatures, starting gas mixture compositions, and degrees of transformation. A study was undertaken to develop a more comprehensive equation for describing the oxidation of SO<sub>2</sub> on vanadium catalysts. The times for which the gas and catalyst are in contact with one another in double- and triple-contact systems at atmospheric pressure (100 kPa) were calculated under the assumption that each stage of the process occurs in accordance with the theoretically optimal temperature curve. The optimal temperatures for various starting gas mixtures and catalysts of commercial grain size were determined for degrees of transformation between 0 and 0.97. An Iskra-1030 computer was used along with existing kinetic equations to analyze the data. Curves of the dependence of contacting time in the first and second stages of catalysis and the total contacting time on the degree of transformation in the first stage of a double-contact system were determined for the catalyst SVD assuming total degrees of transformation of 0.995, 0.998, and 0.999. Similar calculations were performed for the case of a triple-contacting system and IK-1-6 catalyst. The calculations confirmed the superiority of systems with a more even distribution of catalyst between the contacting stages. Systems with three catalyst layers in the first stage and two layers in the second stage were, for example, found to be preferable to systems with four layers in the first stage and one in the second stage. It was established that triple-contacting and triple-absorption systems make it possible to process gases with deeper concentrations of SO<sub>2</sub> to deeper degrees of transformation than double-contact systems do. Calculations performed for the case of a triple-contact system and the catalyst IK-1-6 demonstrated that a degree of transformation up to 0.9995 may be obtained in  $\tau_{min} = 3.19$  minutes. Figures 2, table 1; references 6 (Russian).

**A Comparative Study of Catalysts for the Dehydrochlorination of 1,1,2,2-Tetrachloroethane**

937M0052B Moscow KHIMICHESKAYA  
*PROMYSHLENNOST* in Russian No 3, Mar 92  
pp 137-139

[Article by M.N. Sadogurskiy, T.V. Zavalipinskaya, and O.A. Zayzman; UDC [66.094.46:661.723.641-13]:66.097.322]

[Abstract] Six catalysts for the dehydrochlorination of 1,1,2,2-tetrachloroethane were examined in a comparative study. The catalysts studied were as follows: AGN-1

activated charcoal alone, 10% CsCl on AGN-1, 11% CsCl on KSM silica gel, calcium aluminate alone, 16% CsCl on calcium aluminate, and 16% CsCl + 8% CuCl<sub>2</sub> on calcium aluminate. The kinetics of the reaction of the dehydrochlorination of 1,1,2,2-tetrachloroethane were studied in a 70-ml tube reactor (32 cm long and 1.7 cm in diameter) in an ideal displacement mode. The reactor was heated by a boiling layer of finely dispersed silica gel located in a sleeve between the electric spiral and reaction tube. The temperature in the reactor was kept constant with a precision of +/- 3° C. The prepurified starting 1,1,2,2-tetrachloroethane (purity, /G99%) was fed into the reactor through a vaporizer, where the chlorohydrocarbon was heated to 200° C. The gases leaving the reactor entered a roasting column and were sprinkled with water. Their temperature dropped sharply, and the evolved HCl was trapped. The resultant hydrochloric acid solution was titrated with a 1 N solution of sodium hydroxide, and the organic layer was separated and studied by gas-liquid chromatography. Tsvet-500 and I KhM-80 chromatographs were used for the studies. The AGN-1 and catalyst consisting of 10% CsCl + AGN-1 both proved to have extremely short active lives: After a contact time of only 20 seconds at 300° C, the degree of conversion achieved with the pure activated charcoal dropped from 80% to 50%. The activity of the 10% CsCl + AGN-1 catalyst stabilized at 45-50% after 20 hours of operation. The KSM silica gel resulted in very low degrees of conversion (15.4 to 31.4%). Of the three remaining catalysts studied, pure calcium aluminate proved to be the most stable, and it selectively dehydrochlorinated 1,1,2,2-tetrachloroethane at temperatures of 300° C or lower (degree of conversion at 250° C, 42%; degree of conversion at 300° C, 100%). Figures 3, tables 2; references 11: 7 Russian, 4 Western.

**Zeolite Catalysis—the Basis for Engineering Progress in Oil Refining and Petrochemistry**  
*937M0053A Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL* in Russian No 2, Feb 92 pp 2-4

[Article by B.K. Nefedov; UDC 661.183.6.05:665.6]

[Abstract] Research conducted in the fifties and sixties facilitated the successful use of zeolite-containing catalysts in oil refining and petrochemistry. Zeolite-containing catalysts are used in such basic processes as catalytic cracking and hydrocracking, alkylation, isomerization, disproportionation, and dealkylation of aromatic hydrocarbons. Since the beginning of the 1970's the synthesis of zeolites and zeolite-containing catalysts has been an independent direction in world science. The development and use of high-silica zeolites is the main direction in the field of zeolites and zeolite-containing catalysts both in the former USSR and elsewhere. There are over 40 individual high-silica zeolites belonging to 10 different structural groups. The MF1/MEL type, i.e., the so-called pentasils, are the most studied and most widely used. The following pentasils are produced in the former Soviet Union: TsVK-1 ( $Bu_4NBr$ , N = SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 50 to 1,000); TsVK-11 (aliphatic alcohols, N = 50 to 70);

TsVM (without any organic matter, N = 25 to 50); TsVKN (amino alcohols and hexamethylene diamine, N = 45 to 75); and the ultrasil series (tetraalkylammonium bases and amino alcohols, N = 40 to 200). New pentasil-containing catalysts are effective in processes of deparaffinizing oil fractions to produce products with the required low-temperature and viscosity properties. New processes have also been created for producing jet fuels and winter and Arctic diesel fuels from straight-run and secondary crude oil and for producing industrial, coolant, and motor oils and hydraulic fluids from the plentiful high-paraffin oils of Western Siberia. By combining processes of catalytic reforming and hydrodeparaffination, researchers have been able to produce A-76 and AI-93 high-octane gasolines without TES while reducing the consumption of straight-run fractions. Other important direction in the use of pentasils is that of adding them to cracking catalysts to increase the octane numbers of gasoline fractions and cyclooligomerization or aromatization of low-molecular paraffin and olefin hydrocarbons. Zeolites and zeolite-containing catalysts have made it possible to recover and make rational use of the waste gases of oil refineries and natural and by-product petroleum gases. They have also resulted in the development of processes of 1) selective synthesis of aromatic hydrocarbons, lower olefins, and C<sub>5</sub>-C<sub>10</sub> isoparaffins from nonpetroleum raw material and 2) para-selective catalysis. Many promising new reactions involving pentasil-containing catalysts have been described including the following: alkylation of phenol; chlorination of aromatic hydrocarbons; hydrolysis of esters; oxidation acetoxylation of propylene; disproportionation of ethers; and amination of alcohols by ammonium. It thus appears rather certain that in the coming 5 or 10 years high-silica zeolites and catalysts based on them will be widely used in the domestic oil refining and petrochemical industries to produce motor and jet fuels, oils, and hydraulic fluids from high-paraffin crude oil. References 14: 10 Russian, 3 Western.

**The Connection Between the Acid and Catalytic Properties of High-Silica Zeolite Catalysts of Propane Aromatization**

*937M0053B Moscow KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL* in Russian No 2, Feb 92 pp 20-22

[Article by V.L. Vorobyev, Yu.N. Koshelev, Ye.P. Khvorova, A.A. Kharchenko, and O.M. Oranskaya; UDC 66.097.3:661.183.6]

[Abstract] The link between the acid and catalytic properties of high-silica zeolite catalysts of propane aromatization was studied by way of the example of composites containing type ZSM-5 high-silica zeolite [HZC] and Al<sub>2</sub>O<sub>3</sub> during the process of conversion of propane into aromatic hydrocarbons. Seven specimens of H-HZC and eight specimens of Ga-HZC containing different percentages of zeolite and binder were examined. The Ga-HZC catalysts were produced by impregnating deactivationized zeolite specimens with a gallium nitrate solution and then roasting them in an air stream at 600° C for

12 hours. Gallium was added in the amount of 1.6 wt.-% of the metal. The process of thermocatalytic propane transformation was studied on a flowthrough-type unit made of quartz at atmospheric pressure and a temperature of 560° C. A raw material space velocity of 800 h<sup>-1</sup> was used. Between each experiment the catalysts were regenerated with air at 550° C for 3 hours. The catalytic properties of the specimens were studied in experiments lasting 2 hours. During that time, the catalysts' activity and stability remained unchanged. The reaction products were analyzed by gas-liquid chromatography, and infrared spectroscopy was used to investigate the acid properties of the catalysts. The degree of propane conversion and yield of liquid product both decreased as the content of binder in the H-HZC-Al<sub>2</sub>O<sub>3</sub> catalyst was increased. An increased amount of benzene was noted in the liquid catalyst as the fraction of C<sub>8</sub>-C<sub>11</sub> hydrocarbons decreased. The selectivity of aromatic hydrocarbon formation changed only slightly as the content of binder was increased from 0 to 50 wt.-%. The gallium modified catalysts obeyed the same laws as the H-HZC-Al<sub>2</sub>O<sub>3</sub>. The degree of propane conversion and liquid product yield both decreased as the binder content increased. The nature of the change in the degree of propane conversion in the gallium-modified specimens as the Al<sub>2</sub>O<sub>3</sub> content increased differed from that in the H-HZC-Al<sub>2</sub>O<sub>3</sub> composites, however. The presence of up to 20 wt.-% binder had virtually no effect on propane conversion or liquid product yield. Only at binder concentrations about 45 wt.-% did product yield or propane conversion drop sharply. As the degree of propane conversion decreased, the reaction products formed on the Ga-HZC-Al<sub>2</sub>O<sub>3</sub> catalysts contained less methane, ethane, and C<sub>10</sub>-C<sub>11</sub> aromatic hydrocarbons. No significant changes in the concentrations of propylene, C<sub>4</sub> aromatic hydrocarbons, or C<sub>6</sub>-C<sub>8</sub> aromatic hydrocarbons were observed. Moreover, the degree of propane conversion, liquid product yield, and selectivity of aromatic hydrocarbon formation on the gallium-modified catalysts were all higher than in the nonmodified catalysts. The infrared spectroscopy studies of the catalysts' acid properties established a link between the number and nature of the acid centers and catalytic activity: In the H-HZC-Al<sub>2</sub>O<sub>3</sub> catalysts, as the fraction of binder increased, the number of Bronsted and Lewis acid centers in the catalysts increased and reached a maximum in pure binder. Gallium modification of the zeolite component did not cause a change in the total number of acid centers but did result in their distribution. An analysis of the regression equations for H-HZC-Al<sub>2</sub>O<sub>3</sub> composites demonstrated that in the absence of any modifying additive, the degree of propane conversion is dictated primarily by the number of Bronsted acid centers, and the effect of aprotic centers is insignificant. In the case of gallium-modified catalysts, on the other hand, the link between the degree of propane conversion and the number of acid centers is more complex. It is hypothesized that adding a modifier to the zeolite results in the appearance of aprotic centers of a different nature that affect the process in accordance with a mechanism of not just acid catalysis

but coordination catalysis as well. Figures 2, tables 2; references 6: 5 Russian, 1 Western.

### The Use of Low-Temperature Plasma To Produce and Regenerate Catalyst for Ammonia Synthesis

937M0055A Minsk INZHENERNO-FIZICHESKIY ZHURNAL in Russian Vol 63 No 2, Feb 92 (manuscript received 12 Nov 91) pp 165-171

[Article by G.P. Visokov and G.P. Georgiyev, Electronics Institute, Bulgaria Academy of Sciences, Sofia; UDC 546.171.1:544-44:539.9...15]

[Abstract] Type SA-1 catalyst for ammonia synthesis that ... 1 either been synthesized or regenerated by the plasma-chemical method was studied to determine its physicochemical characteristics. In the case of the regenerated catalyst, samples of type SA-1 catalyst that had been pulverized to particles measuring less than 50 μm were placed in a reactor with "hot walls." Argon (flow rate, 3 m<sup>3</sup>/h) was used as the plasma-forming gas, and argon or pure nitrogen (flow rate, 0.8 m<sup>3</sup>/h) was used as the transporting gas. The particles of deactivated catalyst were in the plasma-chemical reactor for 1 to 5 ms while the temperature in the reaction space ranged from 1,100 to 3,400 K. Ultradisperse catalyst with a particle size of 100 to 300 nm and a specific surface of 3 to 10 m<sup>2</sup>/g were collected in a dust-trapping chamber. The resultant ultradisperse powder was then reduced with hydrogen. The fresh catalyst was synthesized in an oxidation or redox medium. Commercial-grade argon (flow rate, 3 m<sup>3</sup>/h) was used as the plasma-forming gas, and either air or hydrogen (with respective flow rates of 0.8 and 0.5 m<sup>3</sup>/h) was used as the carrier gas. A starting charge was used that resulted in a catalyst analogous to that of commercial SA-1 catalyst (wt.-%) after roasting: Fe<sub>3</sub>O<sub>4</sub> + FeO + Fe<sub>2</sub>O<sub>3</sub>, 94; Al<sub>2</sub>O<sub>3</sub>, 3; K<sub>2</sub>O, 0.8; CaO, 2; and SiO<sub>2</sub>, 0.2. The studies performed established that the plasma-chemical method of regenerating (activating) spent deactivated catalysts of ammonia synthesis is effective. The process entails only two stages, i.e., plasma-chemical regeneration (dispersion) of the catalysts and the formation of granules or tablets. The plasma-chemically regenerated catalysts were regenerated 3 to 5 times more rapidly than catalysts regenerated by the standard method. The plasma-chemical synthesis process also proceeded 3 to 4 times faster than the standard process for synthesizing SA-1 catalyst. The specific surface of the plasma-chemically synthesized catalysts reached 40 m<sup>2</sup>/g, whereas that of the catalyst synthesized by the standard method did not exceed 1 m<sup>2</sup>/g. The catalysts synthesized and/or regenerated under conditions of quasi-equilibrium electric arc low-temperature plasma manifested a 15-25% higher relative catalytic activity than did specimens produced by the standard method. This increased catalytic activity was attributed largely to the greater number of active centers per unit of catalyst mass. The "plasma" specimens were also much more resistant to superheating and deactivation. Figures 4, tables 2; references 17: 14 Russian, 3 Western.

**Stereoselective Hydrogenation of 2-Hexene on Copper Catalysts**

937M0059B Alma-Ata IZVESTIYA AKADEMII NAUK KAZAKHSKOY SSR: SERIYA KHIMICHESKAYA in Russian No 4, Jul-Aug 92 (manuscript received 3 Feb 92) pp 21-26

[Article by A.M. Pak, O.I. Kartonozhkina, G.T. Izdebskaya, T.O. Omarkulov, A.Sh. Kuanyshев, L.R. Krylova, V.N. Shalyukhin, and A.V. Korolev, Organic Catalysis and Electrochemistry Institute imeni D.V. Sokolskiy, Republic of Kazakhstan Academy of Sciences, Alma-Ata; UDC 542.947:547.314:546.56]

[Abstract] The stereoselective hydrogenation of 2-hexene on skeletal copper and applied copper catalysts was studied. The catalysts were prepared by impregnating the carrier with an alcohol copper nitrate solution and then heat-treating it in an air stream and reducing it in a hydrogen current at 573 K for 3 hours. Purified  $MgCO_3$  was used as a carrier. The hydrogenation was performed in accordance with the generally accepted method on a high-pressure kinetic unit at temperatures ranging from 333 to 393 K under pressures of 4 to 8 MPa with ethanol as a solvent. A Chrom-3 chromatograph was used to analyze the hydrogenation products. A number of catalysts resulted in a 100% yield of cis-2-hexene at metal contents of 5, 10, 20, and 30% in the  $MgCO_3$ . Neither varying the pressure from 4 to 8 MPa nor varying the temperature from 333 to 393 K had any effect on the process' stereospecificity. The picture was very different in the case of a 40% Cu/ $MgCO_3$  catalyst, however. After the theoretically calculated amount of hydrogen had been absorbed, only 12% cis-2-hexene and 88% starting compound were found in the catalyst. Further studies established that increasing the amount of copper in the catalyst resulted in a decrease in rate of hydrogen absorption and a decrease in the amount of surface. The order of the reaction was close to zero on all of the applied catalysts, and the activation energy ranged from 40 to 56 kJ/mol. X-ray phase analysis confirmed that all of the copper in the bulk of the catalyst was in a metallic state. Figure 1, tables 2; references 19: 10 Russian, 9 Western.

**Catalysts Based on 12 Series of Heteropoly Compounds of Mo and W in the Reaction of the Oxidation Transformation of  $C_1-C_4$  Alkanes. 1. Partial Oxidation and Oxidation Dehydrogenation of Methane and Ethane**

937M0059C Alma-Ata IZVESTIYA AKADEMII NAUK KAZAKHSKOY SSR: SERIYA KHIMICHESKAYA in Russian No 4, Jul-Aug 92 (manuscript received 6 Feb 92) pp 26-30

[Article by S.A. Tungatarova, B.M. Shingisbayev, A.S. Sars, G.A. Savelyeva, K.Zh. Serikpayeva, and N.M. Popova, Organic Catalysis and Electrochemistry Institute imeni D.V. Sokolskiy, Republic of Kazakhstan Academy of Sciences, Alma-Ata; UDC 542.943.7:547.21]

[Abstract] The catalytic effect of 12 series of heteropoly acids of Mo and W on carriers was studied. The experiments were performed in a flowthrough-type unit in a quartz tube reactor. The concentrations of the reaction mixture's starting components and reaction products were chromatographically analyzed, and the catalysts were prepared by impregnating different carriers with solutions of heteropoly compounds followed by air-drying at 150° C for 5 hours. The catalysts studied proved to be active in the oxidation transformation of  $CH_4$  into  $CH_2O$  and  $CH_4$  and  $C_2H_6$  into  $C_2$  hydrocarbons ( $C_2H_4$  and  $C_2H_6$ ). When all other conditions were identical, the catalysts based on the 12 series of heteropoly acids of Mo were more active in the formation of  $CH_2O$  and less active in the production of  $C_2$ -hydrocarbons than the heteropoly acids of W. At temperatures above 600° C, heteropoly compounds of Mo and W applied to different carriers were active in the oxidation transformation of methane into the following products (at the temperatures indicated in parentheses):  $CH_2O$  (600° C),  $C_2H_6$  (650-750° C),  $C_2H_4$  (750-850° C),  $C_2H_2$  (850-1,000° C),  $C_6H_6$ , and  $C_{10}H_8$  (800° C and above).  $H_2$ , CO, and  $CO_2$  were formed as by-products. These reaction and by-products were determined to be the result of the oxidation pyrolysis of methane. Carriers containing significant amounts of silicon oxide were associated with much higher formaldehyde yields than were carriers based on aluminum oxide and coal. The yield of  $C_2$ -hydrocarbons was found to increase as the concentration of  $CH_4$  in the reaction mixture was increased and as the contact time was reduced to 0.1 s. The catalysts made of the heteropoly compounds of Mo proved to be most active in catalyst reactions in mixtures with a low methane content and with a high content of oxygen (the yield of  $CH_2O$  could reach 12-16% of the methane passed through). Oxidation transformation of ethane was found to occur with the predominant formation of ethane and with a selectivity of ≥90%. Salts were found to be more active than pure heteropoly compounds. Pb-Si-Mo-heteropoly acid showed the greatest activity (a  $C_2H_4$  yield of 530 grams per cubic meter of  $C_2H_6$  with a selectivity above 73% at temperatures of 550°C or more). Figures 2; references 11: 7 Russian, 4 Western.

**Direct Catalytic Oxidation of n-Butane Into Tetrahydrofuran**

937M0060B Kiev TEORETICHESKAYA I EKSPERIMENTALNAYA KHIMIYA in Russian Vol 28 No 2, Mar-Apr 92 (manuscript received 25 Dec 91) pp 159-162

[Article by V.A. Zazhigalov, V.P. Shabelnikov, V.G. Golovatyy, A.I. Pyatnitskaya, and G.A. Komashko, Physical Chemistry Institute imeni L.V. Pisarzhevskiy, Ukraine Academy of Sciences; UDC 541.128.1+547.21]

[Abstract] A study examined the possibility of soft oxidation of n-butane into tetrahydrofuran in the presence of a V-P-O promoted catalyst. A working mixture of 1.7% (vol)  $n-C_4H_{10}$  and 8% (vol)  $O_2$  in He was used to

oxidize n-butane in a flowthrough-type unit. The partial-oxidation products were analyzed on a Chrom-41 chromatograph with a flame-ionization detector. The oxidation products of the n-butane were analyzed on an MI-1201 mass spectrometer by the field ionization/field desorption method. The analyses confirmed the formation of tetrahydrofuran as a result of the oxidation of n-butane on the V-P-O catalyst. The tetrahydrofuran concentration was found to be temperature dependent. It was concluded that tetrahydrofuran may thus be an intermediate product in the stage of the formation of maleic anhydride from n-butane. The possibility of other parallel routes of the formation of maleic anhydride from n-butane was not excluded, however. Figures 2; references 17: 8 Russian, 9 Western.

#### Laws of the Catalytic Reaction of Methanethiol With Methanol in the Kinetic and Diffusion Range

937M0062A Moscow KHIMICHESKAYA PROMYSHLENNOST in Russian No 7, Jul 92 pp 384-386

[Article by V.Yu. Mashkin, V.B. Yakovleva, V.R. Grunvald, B.P. Borodin, and V.I. Nasteka; UDC [661.7:547.269.11]:541.127]

[Abstract] Methanol was reacted with methanethiol to form dimethyl sulfide. The experiments were conducted in a flowthrough-circulation unit at temperatures ranging from 320 to 420° C with initial reagent concentrations of 1 to 12 mmol/l and contact times of 0.02 to 4 seconds in the presence of an aluminum oxide catalyst. The experiments established that on a catalyst fraction with a grain size of 0.25 to 0.5 mm, the reaction occurs in the kinetic range. As the contact time increases, the degree of reagent conversion and dimethyl sulfide yield also increase. The formation of dimethyl ether was also observed; its yield decreased as the degree of methanol conversion increased. On large catalyst grains (2 to 5 mm), the process was found to occur in the intradiffusion range, with the degree of catalyst surface utilization ( $\eta$ ) amounting to less than 0.1. A kinetic equation was proposed for the diffusion range of the study reaction. The results of calculations based on the proposed equation were consistent with experimental data and with literature values for the methanol diffusion coefficient. Tables 2; references 5: 3 Russian, 2 Western.

#### The Effect of Mechanochemical Activation on the Catalytic Properties of an Fe-Cr-K Dehydrogenation Catalyst

937M0062B Moscow KHIMICHESKAYA PROMYSHLENNOST in Russian No 7, Jul 92 pp 386-388

[Article by V.V. Molchanov; UDC 66.094.187.3.002.237]

[Abstract] The effect of mechanochemical activation on the catalytic properties of an Fe-Cr-K dehydrogenation catalyst was studied. The mechanochemical activation was performed on an ARO centrifugal planetary mill in

stainless steel drums with an inner diameter of 60 mm by steel balls measuring 5 mm in diameter. The balls loaded in the drum weighed 0.2 kg, the catalyst loaded in weighed 0.005 kg, the drum had a rotation frequency of 17.5 s<sup>-1</sup>, and an activation time of 900 seconds was used. Specimens of K-22 commercial catalyst were used as controls. A DRON diffractometer with monochromatized radiation and a Q-1500D were used to study the activated catalyst. The catalyst's catalytic activity in the dehydrogenation of n-butenes was determined in a continuous reactor based on the degree of transformation of n-butenes and butadiene selectivity. The reaction products were subjected to chromatographic analysis. The control catalyst specimens began to show signs of catalytic activity at 800 K, whereas the catalyst specimens subjected to mechanochemical activation became active at 673 K. This lower point of onset of catalytic activity was attributed to the formation in the activated catalyst of an active component with a defective crystalline structure. The fact that the activated catalyst was more active than the control at temperatures above 800 K was explained in terms of the higher degree of dispersion of the active component. When the activated catalyst was heated above 880 K, the degree of n-butene transformation fell to the level achieved on the standard catalyst. This was linked to the thermal annealing of the defects in the crystalline structure of the potassium ferrite. Figures 2; references 4 (Russian).

#### Ways of Reducing Irrecoverable Losses of Platinum-Based Catalysts in Bound-Nitrogen Processes

937M0062D Moscow KHIMICHESKAYA PROMYSHLENNOST in Russian No 7, Jul 92 pp 4008-410

[Article by A.Ya. Loboyko, G.I. Grin, I.I. Goncharov, and N.V. Trusov; UDC 661.562:66.094.373]

[Abstract] A study examined ways of reducing irrecoverable losses of platinum-based catalysts in bound-nitrogen processes. Platinoid screens made of No. 2 alloy were used as study objects. The effect that thermochemical activation of platinoid alloy in atmospheres of different gases has in the alloy's surface morphology and selective properties was studied. The catalyst's surface underwent significant changes after the screens were treated in an air atmosphere. Hydrogen annealing results in the same changes in surface properties plus a fundamental change (decrease) in surface concentration of carbon that is evidently responsible for the positive effect of hydrogen annealing on the selectivity of platinoid screens. Another benefit of hydrogen annealing is the high-temperature removal of a number of intermetallic compounds from the platinoid alloy that, like carbon, screen the catalyst's surface. Increasing exposure to hydrogen annealing to 10 minutes was found to reduce

the surface carbon concentration one and a half times. As far as heat-treating platinoid catalyst in other gases is concerned, it may be stated that either a reduced or oxidized medium is required for a positive effect. The studies performed established that preliminary thermochemical activation of platinoid catalyst helps the platinoid catalyst screens created operate longer and with greater selectivity, thereby reducing irrecoverable losses of platinoid catalyst per amount of product produced by using them. Figures 3; references 12: 10 Russian, 2 Western.

#### The Reaction of Isoprene With Aniline on Complex Palladium Catalysts

937M0063C Moscow *IZVESTIYA AKADEMII NAUK RAN: SERIYA KHMICHESKAYA* in Russian No 8, Aug 92 (manuscript received 24 Oct 91) pp 1794-1798

[Article by Ye.A. Petrushkina and L.I. Zakharkin, Elektroorganic Compounds Institute imeni A.N. Nesmeyanov, Russian Academy of Sciences, Moscow; UDC 542.97:66.095.2:547.315.2:547.551]

[Abstract] Isoprene was reacted with aniline on a series of complex palladium catalysts. Monomers with a purity of 99% were used in all of the experiments. The reaction products were subjected to gas-liquid chromatographic analysis on a Model 3700 chromatograph and to ESR studies on a Bruker WP-200SY and Varian VKR-400 spectrometers. The studies established that the reaction of isoprene with aniline on the catalyst system  $Pd(acac)_2 \cdot Ph_3P$  results in a mixture of telomers, i.e., N-(dimethyl-octadiene-2,7-yl-1)anilines and N-(dimethyloctadiene-1,7-yl-3)anilines. On the catalyst system  $Pd(acac)_2 \cdot Ph_3P \cdot CF_3COOH$ , the reaction of isoprene with aniline results primarily in a mixture of adducts, i.e., N-(methylbutene-2-yl)anilines. The reaction of N-methylaniline with isoprene on the catalyst system  $Pd(acac)_2 \cdot Ph_3P \cdot CF_3COOH$  also yields a mixture of adducts, namely, N-methyl,N-(methylbutene-2-yl)anilines. Tables 2; references 7: 3 Russian, 4 Western.

#### Mechanism of Catalytic Reaction of Methanethiol With Methanol in Kinetic and Diffusion Fields

937M0079A Moscow *KHMICHESKAYA PROMYSHLENNOST* in Russian No 5, Jul 92, pp 384-386

[Article by V. Yu. Mashkin, V. N. Yakovleva, V. R. Grunvald, B. P. Borodin, V. I. Nasteka; UDC [661.7:547.269.11]:547.127]

[Abstract] Reaction of methanol with methanethiol was investigated in a circulating setup in temperature range 320-42° C over an aluminum oxide catalyst. When a 0.25-0.5 mm fraction of the catalyst was used, the reaction occurred in the kinetic field: with an increase in the contact time, the degree of the conversion of reagents and the yield of dimethyl sulfide increased. Formation of

dimethyl ether was observed and its yield decreased with increased conversion of methanol. It was concluded that formation of dimethyl ether and of the dimethyl sulfide occurs by independent routes. Reaction mechanism was formulated for these two products with appropriate kinetic equations. Kinetic equation was also developed for the diffusion field of this reaction. Tables 2; references 5: 3 Russian (1 by Western author), 2 Western.

#### Effect of Mechanical-Chemical Activation of Catalytic Properties of Iron-Chromium-Potassium Dehydrogenation Catalyst

937M0079B Moscow *KHMICHESKAYA PROMYSHLENNOST* in Russian No 7, Jul 92 pp 386-388

[Article by V. V. Molchanov; UDC 66.094.187.3.002.237]

[Abstract] One of the ways of increasing catalytic activity of iron-potassium catalyst is to activate iron oxide, which intensifies the interaction of iron oxide with alkali metal carbonates and increases its catalytic activity in dehydrogenation of ethylbenzene. Mechanical-chemical activation of the catalyst was performed in a centrifugal mill with stainless steel drums. The activated and normal catalysts were compared in conversions of n-butenes. Analysis of the experimental results indicated that mechanical-chemical activation, in addition to altering the regulations of the formation of phase composition, impart new catalytic properties by forming active non-equilibrium states with higher free energy. The nature of this active state remains unresolved at present. An opinion was expressed that this is due to the presence of dislocations in the structure of potassium ferrite or by distortion resulting from epitaxial formation of potassium ferrite at the crystallographic edge of iron oxide opened during the mechanical-chemical activation. This opens new ways of increasing catalytic activity by creating defective structures of the active components. Figures 2; references: 4 (Russian).

#### Ways of Lowering Irrecoverable Losses of Platinum Based Catalysts in Bound Nitrogen Technology

937M0079D Moscow *KHMICHESKAYA PROMYSHLENNOST* in Russian No 7, Jul 92 pp 408-410

[Article by A. Ya. Loboyko, G. I. Grin, I. I. Goncharov, N. V. Trusov; UDC 661.562:66.094.373]

[Abstract] Platinum catalysts remain the leading agents in many chemical processes. The growing use of such catalysts and some irrecoverable losses of this metal create a serious concern, because in some cases it is impossible to substitute any other metal. The authors looked at two possible solutions to the problem: a) an increase in the selectivity of the catalyst which could improve the efficiency of the reaction or 2) trapping platinoids in the

reactive gas stream. In this paper the first option, i.e. improvement of the selectivity was covered. One approach is based on the calcination of the catalyst. Experiments were performed to elucidate the mechanism of activation of platinum mesh during the calcination. It was shown that initially the calcination leads to removal of original defects on the surface layer of the catalyst followed by recrystallization of the surface. Current practice does not consider the initial lowering of the selectivity, which is followed by

its increase due to the formation of new active centers in the catalyst. Along with this, at high temperature hydrogen calcination, a number of intermetallic compounds are removed which screen the surface of the catalyst. Thus by proper thermochemical activation of the platinoid catalyst, its use can be extended and it will become more selective. In practical terms this will result in savings of the metallic platinum per production unit. Figures 3; references 12: 10 Russian, 2 Western.

**Small-Capacity Chemistry: Its Technological Aspect**

937M0061A Moscow KHIMICHESKAYA  
*PROMYSHLENNOST* in Russian No 8, Aug 92  
pp 446-451

[Article by L.N. Shkaraputa, V.T. Sklyar, A.V. Kononov,  
and L.A. Tishchenko; UDC [661.7:65.017.3]:  
[66.011.001.57:517]

[Abstract] The value of mathematical modeling when developing even small-capacity chemical-manufacturing processes is illustrated by way of several related examples. Discussed first are reactions of electrophilic complexing of chlorine to unsaturated compounds in water (chlorohydration). The process of developing a mathematical model describing the laws governing the production of chlorohydrin in mixture, intermittent, plug-flow, and semicontinuous reactors by using the postulate of quasi-homogeneity is outlined. Special attention is paid to the procedure for using a mathematical model and optimization criteria to optimize the process of producing chlorohydrins in semicontinuous reactors.

The optimization process described made it possible to significantly improve the indicators of the chlorohydration of 3-thiolene-1,1-dioxide in a semicontinuous reactor (productivity was increased fourfold, and the dichloride content was reduced from 5-7 to 0.1-1%). The procedures followed in using a mathematical model to develop a process to produce a formaldehyde-free preparation to fix the dyes applied to cotton fabric (3,4-dimethoxythiolan-1,1-dioxide) are also described. An algorithm is developed for calculating concentrations and mass flows and for configuring the equipment required to implement the process. Tests conducted at the Glukhovsk Cotton Combine demonstrated that the preparation produced by the process modeled makes it possible to combine the processes of finishing and fixing the active dyes in a print. The air permeability of fabric treated by the new preparation remains virtually unchanged, and the fabric is characterized by good color stability. The cost savings from using 1 metric ton of the new 3,4-dimethoxythiolan-1,1-dioxide preparation is estimated at 1,250 rubles. Figures 3, table 1; references 18: 17 Russian, 1 Western.

**Selected Colloid-Chemical Properties of Lipids**

937M0052C Moscow KHIMICHESKAYA  
PROMYSHLENNOST in Russian No 3, Mar 92  
pp 144-146

[Article by I.N. Zhukov, Yu.V. Remizov, Z.V. Ushakova, and Ye.I. Bogdanova; UDC [661.7:577.175.722].004.82:661.183.123]

[Abstract] Lipids isolated from insulin production wastes were subjected to a study to determine their colloid-chemical properties. The technique of adsorption chromatography on silicon oxide was used to determine the individual types of lipids. Neutral lipids were eluted from the column with chloroform, glycolipids were eluted with acetone, and phospholipids were eluted with methanol. The neutral lipids were then separated in a second column with silicon oxide; the hydrocarbons were eluted with pure hexane, the cholesterol esters were eluted with hexane containing 2% sulfuric ether, the triacylglycerin was eluted with hexane with 5% sulfuric ether, the cholesterol and diacylglycerin were eluted with hexane containing 15% sulfuric ether, and the monoacylglycerin was eluted with pure ether. The hydroxyl, iodine, and acid numbers of all of the lipids were determined to establish their molecular mass. The compositions of all of the lipids studied were found to include various unsaturated compounds, including unsaturated acids. The colloid-chemical properties of the phospho- and glycolipids were studied in accordance with the generally accepted methods; their critical concentrations of micelle formation [CCM] at a water-air interface at 25° C were determined both graphically and conductometrically. The graphic (conductometric) CCM determined were as follows: glycolipids, 0.002 (0.001); phospholipids, 0.015 (0.03); and neutral lipids, 0.0025 (0.0039). As surfactants, the lipids studied were found to have a satisfactory wettability at low concentrations. Phospholipids were found to form the most stable emulsions. The lipid compounds studied formed unstable foams, with the neutral phospholipids forming the best foams. The lipids studied thus proved to be effective surfactants that may find use in different areas of the national economy. Figures 2, table 1; references 4: 2 Russian, 2 Western.

**Special Features of the Carbonization of Nickel Catalysts of Methane Conversion and Their Role in the Development of New Contacts**

937M0052D Moscow KHIMICHESKAYA  
PROMYSHLENNOST in Russian No 3, Mar 92  
pp 149-152

[Article by D.N. Melentyev; UDC 66.097.3.002.237: 661.961.61]

[Abstract] The special features of the carbonization of nickel catalysts of methane conversion must be examined at three levels: the level of interacting molecules and atom groupings; the level of the chemical reaction in and of itself; and the level of the reaction space formed by the

equipment used to conduct the reaction. Whenever the threat of carbonization is estimated, problems always arise because of the uncertainty of the composition of the gas. Purely thermodynamic estimates of carbonization are known to be fundamentally inadequate because of the nonclosed nature of real reaction systems and because of the possible absence of equilibrium between individual stages of the chemical transformation. The predominance of one carbon formation mechanism over another is determined by the qualitative and quantitative make-up of the mixture undergoing conversion and the temperature, pressure, and special features of the surfaces present in the reaction zone. The problems of developing catalysts that are, on the one hand, resistant to carbonization and, on the other hand, highly selective are two separate problems that oftentimes require very different and even contrary development solutions. If carbonization is looked upon solely as a consequence of methane pyrolysis, the goals of increasing catalyst activity and reducing the threat of carbonization do not contradict one another. In the case of nickel catalysts, the existing research and industrial practice indicate that carbon formation decreases as the sizes of the nickel crystallites decreases. By reducing the size of the nickel particles used, it is thus possible to shift the so-called thermodynamic carbon threshold to the region of more rigid process parameter values. Obviously, catalyst activity will increase in the process. Carbon thread growth increases as nickel crystallite size decreases, however. A minimum of two conditions must therefore be met for the formation of threadlike carbon: individualization of the carbon atoms on the surface and a relatively rapid rate of carbon migration into the bulk of the crystallite when compared with the gasification rate. An experimental catalyst, tentatively designated OK, was developed with consideration for these facts. It contained the following (%): NiO, 8, Al<sub>2</sub>O<sub>3</sub>, 92; and CaO, 0. The performance of the OK catalyst was compared with the methane pyrolysis catalyst GIAP-18 (which contains at least 11% NiO, at least 70% Al<sub>2</sub>O<sub>3</sub>, and 8 +/- 2% CaO). At 500° C the residual content of methane in the converted gas amounted to 38.7 vol.-% for the OK versus ≤ 36 vol.-% for the GIAP-18; at 700° C, the residual methane content amounted to 3.6 vol.-% in the case of the OK catalyst versus ≤ 4 in the case of the GIAP-18. The degree of catalyst carbonization amounted to 0% in the case of the OK and 30-50% in the case of the GIAP-18. References 8: 6 Russian, 2 Western.

**A Summary of the Development of the Theory of the Stability of Colloids and Thin Films**

937M0063A Moscow IZVESTIYA AKADEMII NAUK RAN: SERIYA KHIMICHESKAYA in Russian No 8, Aug 92 (manuscript received 23 Apr 92) pp 1708-1717

[Article by B.V. Deryagin, Physical Chemistry Institute, Russian Academy of Sciences, Moscow; UDC 541.18]

[Abstract] The author has summarized his own work on the stability of colloids and thin films beginning with his 1937 publication of the first strict theory of the stability

of weakly charged and highly dispersed lyophobic ashes. The factors affecting the stability of colloids and thin films are systematized and analyzed. The following factors are covered: electrostatic forces, wedging (disjoining) pressure, the adsorption and electronic components of wedging pressure, and fluids' boundary layers and structural forces. Several aspects of the theory of nucleation, i.e., the formation of a new phase, are discussed, including the probability of nucleation rupture of ultrathin (including lipid and molecular) films due to local stretching, the rupture of bilayer films due to

simultaneous mechanical stretching and diffusion of vacancies, and the kinetics of coagulation as a result of the opposing processes of aggregation and deaggregation. The phenomenon of thermoosmosis (i.e., the flow of fluids through capillaries under the effect of a temperature gradient) is explained in terms of the structural and thermodynamic features of fluids' boundary layers. The mechanism of the swelling of frozen soils is discussed in terms of the developing of wedging pressure in the interlayers of water between the ice phase and soil particles. References 46: 23 Russian, 23 Western.

**A Method of Estimating the Probability of the Formation of an Explosive Concentration of Combustible Dust-and-Air Mixture**

937M0052E Moscow KHIMICHESKAYA PROMYSHLENNOST in Russian No 3, Mar 92 pp 183-184

[Article by B.G. Popov, O.V. Serazutinova, and A.A. Gudkov; UDC 614.833.5]

[Abstract] A method is proposed for making an a priori estimate of the probability that an explosive dust-and-air mixture concentration will be reached in a device. The probability that an explosive concentration will be reached may be estimated by using the equations provided together with normal distribution function tables. The equations presented are designed for use in cases where the calculated concentration of the solid combustible phase is less than the lower concentration threshold of flame propagation. The equations and method presented are intended for use in developing safety recommendations. An example of using the method to calculate the explosion risk of a sulfur powder is presented. Figures 2; references 5 (Russian).

**The Effect of Colored Noise on a Particle's Combustion**

937M0055C Minsk INZHENERNO-FIZICHESKIY ZHURNAL in Russian Vol 63 No 2, Feb 92 (manuscript received 13 Aug 91) pp 156-160

[Article by M.V. Tretyakov, Ural State University imeni A.M. Gorkiy, Yekaterinburg; UDC 536.46]

[Abstract] The effect of external noise with a nonzero time correlation (colored noise) on the combustion of a lone particle was studied. The effect of colored noise on both steady-state heterogeneous reaction conditions and on stochastic ignition (spontaneous combustion) of a particle were analyzed in a mathematical model. It was discovered that giving consideration to the finite nature of the radius of the correlations acting on the system of fluctuations yields results that are qualitatively different from the case of white noise. In the case of colored noise (as opposed to white noise), the range of parameters where three combustion modes are possible is expanded. In situations where the determinate theory or theory based on the use of stochastic differential equations with white noise predicts that only kinetic (only diffusion) modes can occur, both low- and high-temperature combustion is also possible under the assumption of colored noise. Colored noise may lead to both the ignition and extinguishment of a particle. The analysis of the steady-state thermal conditions considered indicated that increasing the correlation time  $\tau_c$  results in an increase in the time of a possible transition from a kinetic to a diffusion mode. This difference in the behaviors of systems with white and colored noise was explained in terms of the fact that the correlated process is a process "with memory," thanks to which the object acquires "inertial" properties. An equation for steady-state thermal reaction conditions was derived. Figures 2; references 8: 5 Russian, 3 Western.

**Cathode Processes During the Electrochemical Extraction of Palladium and Tin From Hydrochloric Acid Combined Activation Solutions**  
**937M0056A Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL** in Russian Vol 58 No 7, Jul 92 (manuscript received 15 Aug 91) pp 547-550

[Article by N.A. Shvab, K.A. Kazdolin, L.A. Klimenko, and Yu.S. Dzyazko, Institute of General and Inorganic Chemistry, Ukraine Academy of Sciences, Kiev; UDC 621.357.7]

[Abstract] The methods of voltammetry and preparative electrolysis were used to study the possibility of combined electroprecipitation of Pd and Sn from model hydrochloric acid solutions and combined extraction of Pd, Sn, and Cu from spent combined activation solutions and their rinse waters. An MA-41 anion-exchange membrane was used to separate the electrode spaces of an experimental cell with a pseudo-rarefied layer of inert (glass) particles. Copper plates were used as the cathodes, and platinum or graphite plates were used as anodes. A Pye Unicam SP9-800 atomic-adsorption photometer was used to make the analytical determinations. All of the studies were performed in 1 M NaCl and 2 M HCl. A PI-50 potentiostat with a potential scanning speed of 5 mV/s was used to record voltammograms. The experiments were performed at 20 +/- 2° C. The nature of the currents of the electroreduction of Pd and Sn and the combined discharge of Cu, Pd, and Sn was determined. The experiments confirmed that it is possible to obtain quality combined deposits of metals with rather high current efficiencies at current densities 0.2 to 0.3 the total limiting current. When metals were electrochemically extracted in a pseudo-rarefied layer of inert (glass) particles, it was possible to obtain a residual concentration of Pd in the solution of less than 1 mg/l. Figures 5, table 1; references 14: 10 Russian, 4 Western.

**The Electrochemical Behavior of Magnesium Amalgam in a DMSO Solution**

**937M0059A Alma-Ata IZVESTIYA AKADEMII NAUK KAZAKHSKOY SSR: SERIYA KHIMICHESKAYA** in Russian No 4, Jul-Aug 92 (manuscript received 10 Oct 91) pp 15-21

[Article by I.A. Makarova, A.A. Lange, and S.P. Bakhman, Chemical Sciences Institute imeni A.B. Bekturov, Republic of Kazakhstan Academy of Sciences, Alma-Ata; UDC 13-669.791.5]

[Abstract] The methods of potentiometry, voltammetry, and coulometry were used to study the electrochemical behavior of magnesium amalgam in dimethyl sulfoxide [DMSO]. The electrochemical measurements were taken at a stationary macroelectrode in a glass three-electrode cell equipped with a water sleeve for thermostating. The cell's cathode and anode sections were separated by a porous glass diaphragm. Magnesium amalgam with a surface area of about 1.0 cm<sup>2</sup> and a volume of about 0.8 cm<sup>3</sup> served as the working electrode, a platinum wafer

was used as the auxiliary electrode, and a saturated calomel half-cell served as the standard electrode. The studies were conducted at temperatures of 20, 40, and 60° C while the amalgam and solution were mixed with a glass stirrer at a rate of 400 rpm. The amalgam was prepared from chemically pure M-00 elemental magnesium and R-0 mercury that had been purified by vacuum distillation. Studies of the effect of metal concentration and temperature on peak current established that the magnesium oxidation temperature increases as the magnesium content and temperature increased; at all of the study temperatures the increase in anode currents was directly proportional throughout the entire homogeneity range. The limiting magnesium and amalgam ionization currents were shown to have a diffusion nature. The rate of electrolytic dissolution of inhomogeneous amalgams was shown to be determined by the decomposition rate of the intermetallic compounds of the solid phase, with the process conforming to zero-order reaction laws. The relatively low rate of ionization of the magnesium from the amalgam virtually throughout the entire homogeneity range and the high process activation energy were taken as an indication of the appearance of kinetic impediments to the electrode process at  $C_{Mg} > 10^{-2}$  g-at/l. It was discovered that the ionization process occurs with a large excess voltage as a result of passivation of the surface of the magnesium-amalgam electrode by adsorption layers of the components of the electrolyte used. Figures 3; references 19: 17 Russian, 2 Western.

**The Electrochemical Functionalization of Organic Compounds by "Small" Molecules**

**937M0060A Kiev TEORETICHESKAYA I EKSPERIMENTALNAYA KHIMIYA** in Russian Vol 28 No 2, Mar-Apr 92 (manuscript received 5 Mar 92) pp 97-114

[Article by V.D. Pokhodenko, V.G. Koshechko, V.Ye. Titov, and D.V. Sednev, Physical Chemistry Institute imeni L.V. Pisarzhevskiy, Ukraine Academy of Sciences, Kiev; UDC 541+138+541.515+542.951+542.958]

[Abstract] Original and published research on processes of the electrochemical introduction of "small" molecules (CO<sub>2</sub>, SO<sub>2</sub>, CS<sub>2</sub>, and NO) into organic substrates has been systematized. Special attention has been paid to cathodic carboxylation of halogen-containing aliphatic and aromatic compounds, polymers, and olefins; sulfonylation and carbodithionation of freons; and anodic nitrosation of amines. The likely mechanisms of these processes and the effect of the reagents' nature and electrolysis conditions on the composition and yield of reaction end products have been examined. The overriding conclusion of the review is that the electrochemical functionalization of organic compounds by introducing "small" molecules paves the way for fundamentally new approaches to synthesizing a wide range of different derivatives without any need to use expensive and hazardous reagents. Another benefit of the processes discussed is that they represent a way of recycling CO, CO<sub>2</sub>, SO<sub>2</sub>, nitrogen oxides, and freons.

Despite the extensive progress that has been made in the field of electrochemical functionalization of organic compounds, several important problems regarding the process remain unstudied or only inadequately studied. Included among these problems are the following: the fine points of the mechanisms of the individual processes; the kinetics of the electrode reactions of electrochemical functionalization; the effect of various factors (such as the natures of the electrode, solvent, and background electrolyte and the electrolysis regimen) on the process; and the use of homogeneous and heterogeneous electron transfer agents, gas diffusion electrodes, and solid electrolytes in the functionalization processes. Another prospective research area that appears particularly promising is the creation of "hybrid" processes of activating "small" molecules in electrochemical processes based on the use of familiar heterogeneous and homogeneous catalysts of chemical reactions. Figures 2, tables 5; references 87: 20 Russian, 67 Western.

### Electrochemical of Dechlorination of Anolyte in Chlorine Production Processes

937M0062C Moscow KHIMICHESKAYA PROMYSHLENNOST in Russian No 7, Jul 92 pp 402-404

[Article by O.P. Romashin, N.F. Safronova, I.Z. Altman, and A.F. Mazanko; UDC 661.41:621.3.035.82]

[Abstract] A study examined the cathodic reduction of  $\text{ClO}^-$  and  $\text{ClO}_3^-$  ions in solutions of chlorides in the cathode space of a laboratory electrolyzer. A perfluorinated cation-exchange membrane was used to divide the electrolyzer into an anode chamber with a mercury oxide titanium anode and a cathode space (made of titanium) that contains a cathode made of graphite granules. The anode space was filled with an NaCl solution (concentration, 300 g/l) at a rate sufficient to keep the content of NaCl in the anolyte at 200 g/l. Anolyte (a 200-g/l NaCl solution containing  $\text{ClO}^-$  and  $\text{ClO}_3^-$  ions) was fed into the electrolyzer space. The laboratory electrolyzer was designed to make it possible to change the thickness of the cathode space and, hence, the thickness of the graphite layer. A titanium current lead was used to feed electric current to the cathode space. The graphite granules ranged from 3 to 5 mm in diameter. At current densities above  $15 \text{ A/m}^2$  (for  $\text{ClO}^-$ ) and above  $20 \text{ A/m}^2$  (for  $\text{ClO}_3^-$ ), decreases in the  $\text{ClO}^-$  and  $\text{ClO}_3^-$  concentration in solution of 0.0575 and 0.5 g/l were achieved. Further increases in current density had no effect on the amount of ions reduced. Preliminary acidification of the solutions treated also proved valuable from the standpoint of destruction of chlorine-oxygen ions. These findings were used to develop a new process for electrochemical dechlorination that could be used in a pilot-commercial unit to produce KOH of reagent purity. The new electrochemical dechlorination unit and process proved to offer the following advantages: 1) no need to use expensive and scarce chemical reducing agents and reagents (especially ones containing potassium); 2, the absence of toxic  $\text{SO}_4^{2-}$  ions in the anolyte-brine cycle;

and 3) no need to use alkali to bring the pH of the treated solution to a level of 11.0-12.0 prior to ion-exchange purification (thanks to the alkalization of the treated solution that occurs in the cathode chamber and that may be precisely controlled by the current load). Figures 2, table 1; references 4: 3 Russian, 1 Western.

### The Electrochemical Reduction of Selected Two-Coordinate Phosphorus and Arsenic Compounds in an Aprotic Medium

937M0063B Moscow IZVESTIYA AKADEMII NAUK RAN: SERIYA KHIMICHESKAYA in Russian No 8, Aug 92 (manuscript received 25 Jul 91; after revision 16 Jan 92) pp 1754-1759

[Article by T.V. Troyepolskaya, G.A. Vagina, E.I. Yushkeva, A.S. Ionkin, N.V. Nikolayeva, and B.A. Arbuzov (deceased), Organic and Physical Chemistry Institute imeni A.Ye. Arbuzov, Kazan Scientific Center, Russian Academy of Sciences; UDC 541.138.3:542.91]

[Abstract] The electrochemical reduction of selected compounds of two-coordinated phosphorus and arsenic with a linear structure in an aprotic medium was examined for the first time. Three C-N,N-(dialkylamino)-P-phenylmethylenephosphines (compounds 1, 2, and 3) and C,N,N-(dimethylaminoamino)-As-2,4-di-tert-butyl-6-methyl-phenylmethylenearsine (compound 4) were synthesized and studied. A PU-1 polarograph was used to record voltammograms in  $\text{CH}_3\text{CN}$  against a background of  $1 \times 10^{-3} \text{ M} \text{Et}_4\text{NClO}_4$ . A P-5827M potentiostat was used to perform controlled-potential electrolysis, and a Specord M 80 spectrometer was used to record the infrared spectra of the electrolysis products. The key polarographic characteristics recorded confirmed the irreversibility of the electrochemical reduction process, as well as the presence of significant kinetic constraints in the electrode process. The polarographic data obtained in the experiments performed were insufficient to draw any definitive conclusions regarding the direction of the electrode process. It was hypothesized, however, that the double bond R-E (E = P or As) and the C-E  $\sigma$ -bond activated by the double bond located alongside are possible centers of attack by electrons at the electrode. Likely schemes of the electrochemical reduction of the study compounds were proposed. Specifically, it was concluded that the electrochemical reduction process consists of the decay of the P-E bond of compounds 1, 2, and 4 and with the splitting of the  $\text{C}_{Ar}\text{P}$  bond in the spatially hindered compound 3, after which further chemical transformations of the unstable electrolysis products result in the formation of a wide array of products of their chemical transformation under the effect of oxygen and traces of the moisture present in air. Table 1; references 9: 6 Russian, 3 Western.

### Electrochemical Dechlorination of Chloride Production Anolyte

937M0079C Moscow KHIMICHESKAYA PROMYSHLENNOST in Russian No 7, Jul 92 pp 402-404

[Article by O. P. Romashin, N. F. Safronova, I. Z. Altman, A. F. Mazanko; UDC 661.41:621.3.035.82]

[Abstract] Experimental results were reported of the reduction of  $\text{ClO}^-$  and  $\text{ClO}_3^-$  ions in chloride solutions in the cathode volume zone of the electrolyzer separated by a perfluorinated cation exchange membrane into an anode chamber with ruthenium-titanium anode and the cathode chamber made of titanium with the graphite granule cathode. The experiments showed that at current density above  $15 \text{ A/m}^2$  (for  $\text{ClO}^-$ ) or  $20 \text{ A/m}^2$  (for  $\text{ClO}_3^-$ ), the concentration of both ions was lowered. To achieve a more effective breakdown of the chloroxide ions, the solutions should be acidified. Concentration of the ions

studied had little if any effect on the breakdown of the other ions. The advantages of this electrochemical reduction in dechlorination of the anolyte (a chloride solution saturated with chlorine and containing chloroxide mixtures) are: avoidance of the need to use expensive chemical reducers; absence of  $\text{SO}_4^{2-}$  ions in this process, which form normally when sulfites, sulfides or pyrosulfites are used as reducing agents, and the ability to control pH of the solution by varying the current. Table 1; figures 3; references 4: 3 Russian, 1 Western (by Russian authors).

**Pesticides and the Environment**

*937M0052A Moscow KHMICHESKAYA PROMYSHLENNOST in Russian No 3, Mar 92 pp 131-137*

[Article by N.N. Melnikov; UDC 632.95:504.06]

[Abstract] Pesticides account for 1 million of the 500 million metric tons (i.e., 0.2%) of toxic wastes released into the environment each year. Pesticide use throughout the world continues to increase each year. It should be kept in mind, however, that most modern pesticides break down virtually completely within a single growing season. There has been a trend toward a decrease in the amounts of pesticides used, and the relative amounts of different pesticides used continue to change as safer and more effective pesticides are developed. The use of herbicides made of triazines, amides of various acids, urea derivatives, and aryloxyalkyl carbonic acids and their derivatives is to be discontinued. At the same time, the use of sulfonyl ureas, diphenyl ethers, new heterocyclic nitrogen compounds, and organophosphorus compounds is increasing. No significant accumulation of different classes of herbicides in the environment has been observed. In the area of insecticides, the use of organophosphorus compounds continues to be stable, although some increase in their consumption by 1995 is forecast. Synthetic pyrethroids have also gained widespread popularity in the past 15 years, and the assortment continues to grow. The use of carbamide acid derivatives continues to increase, as does the use of new classes of insecticides and acaricides and heterocyclic sulfur and nitrogen compounds such as 2,2'-dichlorodiphenyltetrazine. DDT, which continues to be used in full measure in China and India, was developed as a replacement for the highly poisonous arsenic compounds that used to be applied in great quantities. The fact that DDT replaced a far more deadly class of compounds and the fact that life expectancy has continued to increase significantly during the 40 years for which DDT has been in use are evidence that DDT is not the absolute evil that it is portrayed to be in the press. The use of polychlorodiphenyls, which are far more toxic than DDT, in insecticides also continues to grow. In the past few years, substances produced by microbiological synthesis as products of microorganisms' vital activity have begun to be used as pesticides. The main trend in fungicides is that of the preponderant development of systemic fungicides (the main users of which are the Western European countries). When assessing the effect of pesticides of the ecological situation, it is important to remember that pesticides decompose relatively quickly before having had the chance to damage regions' inhabitants. It should also be remembered that the development of strains of agricultural crops that are highly resistant to pests has, in a number of cases, resulted in the development of plants toxic to man. The requirements imposed on biological plant protection methods should thus be as stringent as those imposed on chemical methods. Tables 5; references 39: 17 Russian, 22 Western.

**Estimating the Toxicity of Furfural to Water Organisms**

*937M0050B Moscow GIDROLIZNAYA I LESOKHIMICHESKAYA PROMYSHLENNOST in Russian No 1, Jan-Feb 92 pp 21-22*

[Article by A.M. Beym and Ye.A. Zommer; UDC 630\*863:547.724.1:543.06]

[Abstract] Furfural is known to be quite active from a biological standpoint. It causes irritation and nerve paralysis in warm-blooded animals, and public health regulations stipulate that its maximum permissible concentration in the air of industrial workplaces be 10 mg/m<sup>3</sup>. The maximum permissible concentration of furfural established for water reservoirs used for municipal and drinking purposes is 1 mg/l. There are no ecological standards for furfural that give consideration to its toxicity to water organisms, however. Tests were conducted to determine the furfural sensitivity of animals belonging to five different groups of water organisms, including *Daphnia magna*, minnows, roaches, and planaria. The duration of furfural's effect on each of the study animals and average lethal concentration were calculated. The tests conducted indicated that 0.5 mg/l would be a good tentative maximum permissible concentration of furfural in water reservoirs subject to further experimental verification. The research conducted also provided indirect evidence of the formation of by-products of the spontaneous decay of furfural. After 15 days, the toxic properties of the study solution, which contained furfural in a concentration of 35 mg/l, initially decreased, then increased once again, and finally culminated with the complete detoxification of the solution between day 15 and day 20. Additional research will be required to determine an actual final maximum permissible concentration, as well as to identify any toxic-genetic hereditary effects that furfural may have. Table 1; references 5: 4 Russian, 1 Western.

**A New Ecologically Pure Process for Producing AMR Oligomer Modifier**

*937M0058B Moscow KAUCHUK I REZINA in Russian No 3, Mar 92 pp 5-8*

[Article by V.M. Sokolik, V.S. Kutyanina, O.S. Yefimova, and B.L. Litvin; UDC 678.045.12]

[Abstract] The modifier RU is currently used to increase the adhesion of rubbers to reinforcing materials. Problems with its production have arisen because of difficulties in obtaining enough imported resorcin. A new modifier that can be made from domestic oligomer materials has been developed. This new modifier, designated AMR, is intended to improve the adhesion of sheathing rubbers to textile and brass-plated steel-cord (especially steel-cord subjected to the effects of high temperatures and corrosive media). The process developed to produce AMR oligomer modifier is ecologically pure and provides a 99% product yield without the generation of any wastewaters. AMR is produced in two stages. First, its

components are mixed in a mixer with stainless steel Z-shaped blades at a water temperature of  $75 \pm 5^\circ\text{C}$  in the sleeve in order to produce a homogeneous mass. In the second stage, thickening agent is added to the intermediate product in portions (at the same heating water temperature) until a homogeneous mass is produced. The modifier is then granulated on a GFSh-45 granulator in the presence of 7% liquid petroleum paraffins. The draw die is heated with water that has been heated to  $75 \pm 5^\circ\text{C}$ . The granules are cooled by a cool air stream, crushed to a length not exceeding 30 mm, and packaged. This process has been used at the Ivano-Frankovsk Fine Organic Synthesis Plant to produce a test batch (150 kg) of AMR modifier that was then tested under actual production conditions at the Dneproshin Production Association at the pilot-production plant of the NIIShP [not further identified]. Rubbers produced with AMR modifier in place of RU modifier had better adhesion properties (especially when subjected to steam-air and salt aging, in which case their adhesion properties were 1.5 to 2 times as good as those of the rubber with the RU modifier) and were more resistant to thermal aging. The rubbers made with AMR modifier were more effective in rubber mixtures that come into contact with 28L22 steel-cord. The advantages of AMR over RU were even greater under conditions of dynamic tests. Further tests established that in cord rubberizing compounds it is possible to replace RU modifier with AMR without any sacrifice of the level of physicomechanical or adhesion properties; however, a 300% decrease in tensile stress occurs, thus indicating a need to correct the content of vulcanizing group components in rubber mixtures with AMR modifier. A prototype unit with a capacity of 100 metric tons/y is now being installed at the Ivano-Frankovsk Fine Organic Synthesis Plant to produce AMR modifier by the new process. A toxicology analysis of AMR performed at Ivano-Frankovsk Medical Institute established that it belongs to class 3 of toxicity group 4. Tables 3.

#### **Ion Exchange Purification of Ammonium Containing Waster Waters Using Weakly Acidic Cation Exchange Resin SG-1m-2**

937M0079E Moscow KHIMICHESKAYA PROMYSHLENNOST in Russian No 7, Jul 92 pp 411-412

[Article by V. V. Shatalov, I. V. Nikitin, M. V. Kitayeva, V. F. Sinichenkov; UDC 628.543.142:66.094.94]

[Abstract] Experimental investigation of the sorption properties of cation exchange resin SG-1m-2 was carried out under laboratory conditions using model solutions imitating the composition of the condensed material obtained from evaporation of ammonium nitrate and nitroammophos. The pH of this material was in the range of 9.15-11.12 and the concentration of ammonium ions was 0.48-2.55 g/l. The contact with SG-1m-2 catalyst was performed under static and dynamic conditions with the ratio of the exchange resin to solution being 1:1,000. The cation exchange resin was regenerated with

a 10% nitric acid solution. Experiments showed that SG-1m-2 exhibited a high exchange capacity for the ammonium ion at pH greater than 11.0. Lowering the pH to 10.9 decreased this capacity from 2.7 to 1.08 mg-equiv/ml. It was concluded that SG-1m-2 could be used effectively in purifying effluent from ammonium ions. Technical and economical indices could be developed for the purification plants after large scale experiments. Figures 7; references 5: 3 Russian, 2 Western.

#### **Mechanism of Dust Formation and Dust Emission In Drum Granulators-Driers. 1 Communication**

937M0079F Moscow KHIMICHESKAYA PROMYSHLENNOST in Russian No 7, Jul 92 pp 421-422

[Article by N. V. Vasenin, A. A. Kuznetsov; UDC 541.18.04]

[Abstract] Granulators-dryers represent currently the leading sources of environmental pollution resulting from their expanded use. Intensive heat and mass exchange processes lead to massive gas emissions carrying dust formed during their operations. The dust is formed because of the drying out of pulp drops which form during the dispersal step. Mathematical formulae were developed for calculating the dust removal and its concentration at the exit from the granulator-drier. Overall, by lowering of the air pressure in the nozzle and increasing the number of blades, their dimensions, the drum filling coefficient and the rate of its rotation it should be possible to decrease dust emission. Upon comparison with experimental data, the calculated values for dust emission were some 20-50% lower. Table 1; figures 3; references: 6 (Russian).

#### **Calculation of Short Term Emission Characteristics of Contaminants From Annular Slot Nozzle Under Calm Conditions**

937M0079G Moscow KHIMICHESKAYA PROMYSHLENNOST in Russian No 7, Jul 92 pp 423-427

[Article by V. I. Romanov; UDC 614.712.001.24]

[Abstract] At the plants working with highly toxic combustion products, gas purification equipment is used through which gasses must pass before their emission into the atmosphere. Depending on the height of the stack, the ambient temperature, wind velocity, etc., the shape of the emission cloud will differ. A system of equations was developed for various conditions listed above. Graphical presentations were provided for short term emission lasting 1-20 sec, for different coefficients of entrapment and different initial gas temperatures. Other graphs represented the climbing rate of the emission as a function of the initial gas temperatures or of its superheating, relative air humidity, etc. Figures 6.

**A Technology for the Molecular Design of Supramolecular Compounds**

937M0048A Moscow ZHURNAL FIZICHESKOY KHIMIYA in Russian Vol 66 No 1, Jan 92 pp 25-32

[Article by V.Ye. Kuzmin and D.V. Pozigun; UDC 541.63:547.13]

[Abstract] A new strategy has been proposed for the molecular design of supramolecular compounds ("guest-host" systems). The underlying principle of the new process is that of using chelate fragments for the template assembly of the "host" around the "guest." The new design scheme calls for complementary joining of the molecules forming a supramolecular compound in such a way that the steric requirements of the "guest" are consistent with the steric capabilities of the "host," which may in turn be formalized in the form of special charts. A six-step design process is outlined. The first step entails analyzing the form of the molecules of the "guest" to find those active centers or regions (fragments) of the guest that participate in bonding with synthetic acceptors. The second step entails selecting (either empirically or through quantum chemistry calculations) the functional groups that will actually bind the centers of the future host-molecule to provide optimal interaction between the guest molecules and synthetic acceptors. In the third step a decision is made as to how to join the host's active centers to form synthetic receptors, which is to say that the initial selection of the synthetic receptors' topology is made. In step 4, the final selection of the receptor topology is made. In the fifth step the molecular chains are individualized so that their structure will provide the necessary length and conformation rigidity (flexibility). The process culminates in step 6 with the assembly of a receptor from the active centers and molecular chains in the guest's matrix. The ultimate purpose of the new molecular design process is to serve as a component in some future expert system that will permit the computer-aided molecular design of supramolecular compounds. Several examples are provided to illustrate the use of the proposed molecular design approach in designing coordination compounds. It is emphasized that the new molecular approach is still in the initial design stage. Figures 2, table 1; references 5 (Russian).

**Contact Stabilization of Skeletons and Molecules of the Host in "Guest"- "Host" Systems**

937M0048B Moscow ZHURNAL FIZICHESKOY KHIMIYA in Russian Vol 66 No 1, Jan 92 pp 118-125

[Article by Yu.A. Dyadin and N.V. Kislykh, Inorganic Chemistry Institute, Siberian Department, USSR Academy of Sciences; UDC 541.123:541.49:541.572.7]

[Abstract] An analysis of the structure, stoichiometry, and stability of molecular clathrates revealed that the effect of a "guest" subsystem on a "host" subsystem associated with a nonvalence (contact) "guest"- "host" reaction may be subdivided into four types depending on

the initial stability of the host subsystem. The first of these four subtypes consists of solid solutions based on the starting modification of the host form. These solutions may be stable at a temperature higher than the melting point of the starting host if the complete skeleton is thermodynamically stable. In the second subtype a new berthollide-type chemical individuum forms if the clathrate skeleton is a metastable modification of the host (the classical case). In the third subtype, the clathrate has a constant composition over a wide variance of equilibrium conditions if the complete skeleton of the host is absolutely unstable (labile). The fourth reaction subtype is the same as the third but without a guest. Not only is the skeleton labile, but the host molecule is as well. The analysis performed demonstrates that in cases of different relationships of guest and host molecules in a system, changes in the nature of packing and the formation of several clathrate structures are not the only phenomena to occur; the host molecules themselves also undergo significant restructuring. Two clearly unequal subsystems may thus be identified in clathrate compounds: a relatively rigid host (that shares many of the attributes of a crystal body) and a mobile guest (characterized by the attributes of a liquid or gaseous state). Contact stabilization results in different pictures depending on just how independent the host subsystem is. The lower the stability of the skeleton, the narrower the region of homogeneity and degree of filling of the cavities close to 1. When a host skeleton is entirely unstable without a guest, stabilization occurs when the cavities are fully occupied, and the compound has a constant composition throughout the entire stability range corresponding to that degree of filling. Yet deeper instability of the host skeleton is associated with the lability of the host molecules themselves in the absence of guest molecules. The phenomenon of stabilization of a molecule that is nonexistent in and of itself thanks to nonvalence reactions with other molecules is termed contact stabilization of molecules. Figures 8; references 23: 17 Russian, 6 Western.

**Use of the RISM Theory To Calculate the Vaporization Heat of Liquid Hydrocarbons**

937M0048C Moscow ZHURNAL FIZICHESKOY KHIMIYA in Russian Vol 66 No 1, Jan 92 pp 137-139

[Article by S.K. Talitskikh and P.G. Khalatur; UDC 541.64:539.199]

[Abstract] Integral equations of the theory of liquid are used to calculate the vaporization heat for methane, propane, n-butane, benzene, and 1-butene. The calculation method is based on the RISM model, according to which the potential of the interaction of two molecules is looked upon as the sum of the interactions between all of the force centers. The calculated values are shown to be in good agreement with experimental data (no discrepancies of more than 5% were found). The hidden vaporization heat for densities and temperatures corresponding to boiling points at different pressures were

also calculated. The slight differences between the calculated and experimental results that were observed were explained in terms of the change from an infinite integration interval to a finite interval. An analysis of the results revealed that the calculated results depend significantly on the geometric parameters of the models used (bond lengths and valence angles) as well as on the parameters of the atoms' interaction potentials. The calculation method used is said to require less computer time than the conventional Monte Carlo and molecular dynamics methods do. Tables 3; references 3 (Western).

### **Hydrogenated Colophony—A New Flux for Field Soldering**

**937M0050A Moscow GIDROLIZNAYA I LESOKHIMICHESKAYA PROMYSHLENNOST**  
in Russian No 1, Jan-Feb 92 pp 12-13

[Article by S.R. Kushnir, B.A. Radbil, N.I. Matveyev, N.G. Sergeyeva, Ye.A. Vakhlamova, Ye.V. Chuykova, and V.I. Savnykh, Wood Chemistry Industry Central Scientific Research and Design Institute; UDC [630\*866.1.002.6:665.947.83].004.14]

[Abstract] Fluxes containing the natural rosin colophony are widely used for erection or field soldering with low-temperature solders. All existing colophony-based fluxes (FK, FKSp, FKEt, etc.) have a low fluxing activity (a relative activity of about 1). Different activating additives are used to boost activity. The great drawback of all currently used colophony fluxes made from gum rosins, including the activated ones, is their susceptibility to corrosion because of the electroconductive impurities they contain. OK-5 prepurified colophony (TU 13-4000177-154-83) is free of such shortcomings. Its physicochemical indicators and chemical composition are similar to those of the pine gum rosins obtained by the generally accepted method; however, it contains far fewer chemical impurities and thus has a significantly lower electric conduction than gum rosins do. The pilot plant of the Wood Chemistry Industry Central Scientific Research and Design Institute has begun producing OK-5 colophony in limited quantities sufficient to meet 5 to 10% of the demand at instrument making enterprises. Hydrogenated OK-5 is also now being produced at the OmskKhimprom Production Association. That hydrogenated OK-5 is a solid transparent glassy substance with a softening temperature no lower than 66°C, an acid number of no less than 166 mg KOH per gram of product, and no more than 5 wt.-% resin acid with conjugate double bonds. It dissolves well in ethanol, xylol, benzene, acetone, and ethyl acetate, and it has a fluxing activity with respect to gum rosin of 1.2 to 1.4 at soldering temperatures of 200 to 350°C. Tests of the hydrogenated OK-5 colophony produced at the OmskKhimprom Production Association have demonstrated that it has a higher activity than either gum rosin or purified OK-5 colophony. Furthermore, its elevated fluxing activity at reduced soldering temperatures (200 +/- 10°C) makes it suitable for use in automatic erection

soldering. Hydrogenated OK-5 is, for all practical purposes, free of electroconductive impurities and adheres to copper surfaces without peeling or cracking. It manifests good corrosion resistance and does not cause solder to spatter. It is anticipated that using the new hydrogenated OK-5 colophony will result in a savings of 60,000 rubles per ton of hydrogenated colophony thanks to a decrease in the labor and material costs associated with the need to wash products after field soldering. This savings projection does not even give consideration to the better quality and reliability of products produced by using the new flux. Tables 2; references 3 (Russian).

### **Macrokinetics of the Self-Excited Wave Mode of Synthesizing Organic Powders in a Condensed Phase. 1. Dynamic Studies of the Self-Propagating Synthesis of Organic Powders in a Condensed Phase**

**937M0055A Minsk INZHENERNO-FIZICHESKIY ZHURNAL** in Russian Vol 63 No 2, Feb 92  
(manuscript received 17 Oct 91) pp 131-139

[Article by A.D. Ubortsev, B.M. Khusid, Z.P. Shulman, A.G. Merzhanov, and V.A. Mansurov, Institute of Heat and Mass Transfer imeni A.V. Lykov Academic Scientific Complex, Byelorussian Academy of Sciences, Minsk, and Structural Macrokinetics Institute, Russian Academy of Sciences, Chernogolovka; UDC 536.46.5.24:541.128]

[Abstract] A study examined the physicochemical transformations occurring in heterogeneous condensed media in a self-excited wave mode of the propagation of exothermal reactions of organic powders. Specifically, the processes of self-propagating high-temperature synthesis, combustion of pyrotechnic compositions, and self-propagating synthesis in organic mixtures were compared. The studies were conducted in a specially developed unit that included a reactor, a matrix of temperature and electrochemical sensors, and an automated scientific research system based on the IVK-6 system. Unlike conventional contact thermometry methods and equipment, the new experimental unit provided real-time measurements of spatiotemporal temperature distributions, electric conduction, and potential differences in the reactor. The starting mixture was heated by a plane Nichrome spiral with 10-s pulses to a temperature of 200°C in a quartz glass cylindrical reactor. The measurements were taken at a point where the front velocity had already stabilized and did not depend on ignition conditions. An automated measurement system based on an SM-1300 in the CAMAC standard was developed to measure the processes occurring at the wave front. The thermophysical properties of the study objects, i.e., malonic acid and piperazine, and their reaction products were measured and analyzed from the standpoints of the dynamics of the thermal processes, electrophysical transformations, and stages of the self-excited wave process occurring during the reaction. The changes in electrophysical parameters that developed in the waves were directly linked to phase, structural, and

chemical transformations. Four stages of the reaction process were identified and discussed ( $T < 100^\circ\text{C}$ ;  $100^\circ\text{C} \leq T \leq 130^\circ\text{C}$ ;  $130^\circ\text{C} \leq T \leq 155^\circ\text{C}$ ; and  $mF155^\circ\text{C}$ ). A qualitative difference between the synthesis of powders of one and the same dispersion in a calorimeter and in a self-excited wave mode was discovered: self-propagating synthesis occurs in two stages (the sequential melting of the components), whereas synthesis in a calorimeter occurs in a single stage (the melting of piperazine). Figures 6, tables 3; references 21: 19 Russian, 2 Western.

**A Study of the Mechanical and Thermophysical Properties of Composite Materials Based on "Black Binders" To Optimize the Process of Their Joining With Adhesives**

937M0055B Minsk INZHENERNO-FIZICHESKIY ZHURNAL in Russian Vol 63 No 2, Feb 92 (manuscript received 28 Aug 91) pp 151-153

[Article by N.I. Ivanova, V.V. Kharitonov, and V.Ye. Ivanov, Gomel Polytechnic Institute; UDC 691-419.3:699.82:69.024.15]

[Abstract] The thermophysical and physicotechnical properties of Mastrum fused bitumen roofing felt were studied on an instrument (TsT-3) developed at the Thermal Physics Institute of the Ukraine Academy of Sciences to determine their thermal conductivity by the plate method. Individual samples of the fused bitumen roofing felt and bundles thereof were subjected to studies in which the average temperature was varied over time so that a changing heat flux was directed along each specimen from top to bottom. The fused bitumen roofing felt's cardboard base layer was the greatest contributor to thermal resistance (about  $1.665 \times 10^{-2}\text{ m}^2\text{K/W}$ ). The contribution of the layers of bituminous varnish was much lower (about  $1.53 \times 10^{-3}\text{ m}^2\text{K/W}$ ). The resistance of the air interlayers was rather great and was estimated at somewhere on the order of  $3 \times 10^{-3}\text{ m}^2\text{K/W}$ . These results indicate that as the number of layers in a bundle is increased, the thermal conductivity of that bundle increases, and the thermal conduction of the bituminous varnish begins to play a greater role. When the bitumen layer melts, the paper base is impregnated with the varnish, and threadlike channels of bitumen form in the base, thus helping to increase the thermal conductivity of multilayer bundles. Good quality fusion was obtained when a pressure of  $1 \times 10^3\text{ N/m}^2$  and a temperature of  $50^\circ\text{C}$  were used during the gluing process. The studies further established that there is no need to heat the mastic to  $250^\circ\text{C}$  or test its quality during the gluing process. It was recommended that temperatures of  $80$  to  $110^\circ\text{C}$  combined with a pressure of  $1 \times 10^3\text{ N/m}^2$  be used in the construction industry when gluing fused bitumen roofing felt. Figures 2; reference 1 (Russian).

**Cryochemical Synthesis and Magnetic Properties of Highly Dispersed Powders of Superconductors  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$**

937M0066A Moscow NEORGANICHESKIYE MATERIALY in Russian Vol 28 No 9, Sep 92 (manuscript received 31 Jul 91) pp 1887-1891

[Article by P. Ye. Kazin, V. P. Shabatin, V. I. Pershin, Moscow State University imeni M. V. Lomonosov; UDC 542.9]

[Abstract] Production of HTSC materials with specific properties faces many problems. Solid body preparative methods were developed in which the homogeneity of the distribution of components could be controlled. To be able to regulate microstructure of ceramics, often highly dispersed powders had to be used with application of cryochemical synthetic methods. This report covers the synthesis and results of magnetic studies of ultra-dispersed superconductor powders  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  obtained by a cryochemical method. Analysis of experimental results showed that magnetic characteristics of high temperature superconductors obtained from ultra-dispersed  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  powders are significantly modified. This fact indicates the feasibility of using the cryochemical synthesis to obtain yttrium-barium cuprates in ultra-dispersed state which then can be used in the technology of film, ceramic and other polycrystalline materials. Table 1; figures 3; references 10: 3 Russian (1 by Western author), 7 Western.

**Effect of Antimony on Superconducting Properties of Yttrium, Bismuth and Thallium Cuprates**

937M0067A Kiev UKRAINSKIY KHIMICHESKIY ZHURNAL in Russian Vol 58 No 2, Feb 92 (manuscript received 3 Jul 91) pp 599-603

[Article by S. A. Nedilko, T. P. Lishko, I. V. Golubeva, N. V. Anshukova, Kiev University; UDC 537.312.62:541.451:546.66]

[Abstract] Currently there are many active studies on doping high temperature superconducting ceramics (HTSC) obtained in the systems  $\text{Y}-\text{Ba}-\text{Cu}-\text{O}$ ,  $\text{Bi}-\text{Sr}-\text{Ca}-\text{Cu}-\text{O}$ ,  $\text{Tl}-\text{Ba}-\text{Ca}-\text{Cu}-\text{O}$  with other elements. The goal of this work was to evaluate the effect of addition of antimony on superconducting properties of such ceramics. Antimony-containing HTSC materials were obtained by chemical homogenization methods combined with ceramic technology. Addition of antimony has a minimal effect on superconducting properties of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ , it facilitates formation of a high temperature phase in Bi samples ( $\text{Bi}_{2-x}\text{Sb}_x\text{Sr}_{2.5}\text{Ca}_{0.5}\text{M}_2\text{O}_8$ ) and lowers the temperature of superconducting transition in the Tl-system ( $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ ). The compositions obtained are multiphasic. Parameters of elementary cells were calculated for these superconducting phases. Table 1; figures 3; references 15: 4 Russian, 11 Western.

**Mechanism of Current Forming Process in Conducting Polymers of Polyaniline Type**  
**937M0067B Kiev UKRAINSKIY KHMICHESKIY ZHURNAL** in Russian Vol 58 No 2, Feb 92  
 (manuscript received 26 Sep 91) pp 651-653

[Article by S. V. Chivikov, V. Z. Barsukov, A. V. Gorodyskiy, Institute of General and Inorganic Chemistry, Academy of Sciences of Ukraine, Kiev; UDC 541.135.5]

[Abstract] Conducting polymers, also known as "organic metals", are interesting, novel materials that can be used as chemical current sources and applied in electronics. These poly- $\pi$ -conjugated substances include polyaniline, polyacetylene, polythiophene, polyphenylene, polypyrroles etc. There are several views on the mechanism of current forming processes in such materials through intermediate formation of cation radicals, various complexes, polarones, etc., but none seem to adequately explain the observed characteristics of electrochemical behavior of conducting polymers. In the course of this work, it has been shown that this current forming process is directly connected with charge-discharge capacity of double electric layer, exceptionally high in such materials due to the well developed effective surface contact of conducting polymer macromolecules with the electrolyte. Based on the predominating concepts about the structure of conducting polymers, relationships were proposed for evaluation of double electric layer capacity, and the galvanostatic character of the charge-discharge curves was explained along with other characteristics of electrochemical behavior of electrodes based on conducting polymers. Figure 1; references 5: 2 Russian, 3 Western.

**Water-Proof Coatings With Adhesive-Inhibitory Protective Action**

**937M0071A Moscow LAKOKRASOCHNYYE MATERIALY I IKH PRIMENENIYE** in Russian No 4, Jun-Jul 92 pp 14-17

[Article by V. G. Shigorin, L. A. Poluektova, V. I. Rudich, A. G. Volnitsov, N. I. Fomina, I. Yu. Molotov; UDC 667.657.233:620.197.3]

[Abstract] This actually is a review type article summarizing practical experience in the use of various waterproof anticorrosive materials. The effectiveness of anti-corrosive coatings depends on the mechanism of their protective action against various corrosive factors. The principle of the adhesion-inhibition mechanism of the protective action of polymer coatings is based on conversion of the surface of the material being protected into an adsorption passive state. This is achieved through adsorption of active ingredients such as film forming materials, specific modifiers, setting agents, etc. The adhesive interaction may block active centers of the metal surface making them inaccessible to the corrosive medium. Its stability assures long lasting protection in water and neutral electrolytes. The data reflecting a

relationship between the mechanism of surface protection and operational properties have been tabulated for a number of coatings. In principle, it is possible to predict the reliability and long term service of anticorrosive coatings on the basis of their mechanism of protective action applied to specific conditions. Tables 2; references 20: 17 Russian, 3 Western (2 by Russian authors).

**Paint and Varnish Materials for Marine Coatings**

**937M0071B Moscow LAKOKRASOCHNYYE MATERIALY I IKH PRIMENENIYE** in Russian No 4, Jun-Jul 92 pp 19-21

[Article by A. V. Sheshukov, M. V. Simanovich, E. F. Itsko, V. P. Kirpichev, Scientific Production Association "Pigment"; UDC 667.637:233.3:629.12.011.71]

[Abstract] The first part of a literature review was presented, the continuation of which will follow in the next issue. Domestic ship building industry shows an acute shortage of reliable paint and varnish materials which would protect better against corrosion and barnacle formation. The paints are normally designed for specific applications: under water utilization, variable exposure around the water-line, above the water ship sides and the deck covers. The corrosion rate in sea water is determined by its chemical composition, temperature and the speed of the ship. Water pollution and accumulation of sea organisms on the hull also intensify the corrosion process. Review of individual paints and varnishes with specific application and requirements was then reported, covering some of the domestic and foreign productions. Routinely the base of the cover was noted, its application, the country of origin and the name or code for the specific coating. No tables, figures or references.

**Optical Properties of White Pigments and Coatings Based on Them Irradiated with 500 keV Protons**

**937M0071C Moscow LAKOKRASOCHNYYE MATERIALY I IKH PRIMENENIYE** in Russian No 4, Jun-Jul 92 pp 26-28

[Article by N. A. Shcherbakova, A. G. Kotov, N. I. Kochnev; UDC 667.622'613.2'

[Abstract] Thermally regulated paint-varnish coatings with high reflective property are used widely in situations involving exposure to ionizing radiation. Integral coefficients of the adsorption of sun rays  $\alpha_s$  were determined for such samples prior to and after irradiation with 500 keV protons. The following metal oxides were used in the experiments: ZnO, SrO, MgO, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub> and the coatings with following film forming reagents: fluoroplast, vinyl chloride, polyvinyl acetate, polyvinyl butyrate, acrylic, melanin-formaldehyde and silicon-organic materials. Experiments showed that the reflective ability of these pigments varies from one

reagent to another. All of them showed a shift in characteristic absorption towards the visible region which could indicate formation of crystalline structure defects. The most stable paint-varnishes were those based on materials containing  $TiO_2$ . It was of interest to note that radiation resistance is determined by radiation stability of the pigment as well as by its catalytic activity. Tables 2; figure 1; references: 2 (Russian).

**Oil Paints and Enamels Containing Zinc Oxide Pigment Obtained From Zinc Containing Wastes**  
**937M0071D Moscow LAKOKRASOCHNYYE MATERIALY I IKH PRIMENENIYE in Russian No 4, Jun-Jul 92 pp 48-50**

[Article by V. M. Laptev, G. M. Gayduchenya, F. I. Akhmarov, V. O. Smirnov, O. K. Kamalov, Kirov Polytechnical Institute; UDC 667.633.24: 667.622.14.712:628.31]

[Abstract] In connection with continuous depletion of the traditional sources of zinc, it became necessary to look for secondary zinc containing materials which normally are treated as waste. Tests were made of hydro-metallurgical reprocessing of zinc containing slag for its reuse as zinc oxide in production of pigments. Four ways of producing zinc oxide were tried: 1) slag leaching with a sulfuric acid solution followed by precipitation of zinc carbonate with ammonium carbonate and calcination; 2) extraction with nitric acid; 3) leaching with a solution of sodium hydroxide followed by precipitation of ZnO with dilute nitric acid and 4) extraction with ammonium carbonate and ammonia followed by evaporation and calcination. All zinc oxide samples thus obtained showed elevated oil content but otherwise corresponded to B

grade of the higher brand normally used in industry. Paints and enamels produced from such ZnO were tested and showed clear, light tones; all of them dried well and exceeded the stability standards. Tables 2; references: 10 (all Russian, 3 by Western authors).

**Use of Maleic Anhydride and Polyethylene Terephthalate Production Waste for Production of Enamels**

**937M0071E Moscow LAKOKRASOCHNYYE MATERIALY I IKH PRIMENENIYE in Russian No 4, Jun-Jul 92 pp 43-45**

[Article by V. P. Savelyanov, A. G. Gonorskaya, T. V. Balachintseva, O. V. Shinkarenko, M. G. Golofayeva, Novomoskovskiy Branch of Moscow Chemical-Technological Institute imeni D. I. Mendeleyev; UDC 667.62.6 + 678.664/.674(tab)]

[Abstract] The use of waste material from organic manufacturing of paints and enamels is advantageous economically and ecologically. It was of interest to find possible application for waste material containing polybasic acids and polyatomic alcohols for production of polyester and polyurethane enamels. Residual waste from the production of maleic anhydride contain anhydrides of maleic and phthalic acids as well as sulfuric acid. The waste products of the synthesis of polyethylene terephthalate contain ethylene glycols and terephthalic acid esters. Attempts to use these materials in standard production of polyester resins were successful. The products obtained could be used even for inside painting of various facilities, wood and metal objects, etc. Because of their dark colors such products would be somewhat restricted in decorative applications. Tables 4; references: 7 (Russian).

**Adsorption Kinetics on Melamine Resin Filters**

**927M0238C Moscow ZHURNAL PRIKLADNOY KHIMII** in Russian Vol 65 No 2, Feb 92 (manuscript received 02 Nov 90; in final form 1991) pp 327-331

[Article by A.B. Oreshkov, N.V. Katushkina and V.M. Kolikov, State Technical University, St. Petersburg; UDC 543.544:047.12]

[Abstract] Key factors affecting rate of adsorption to melamine filters were assessed through a study on the adsorption kinetics of human serum albumin (HSA) and  $\text{MoO}_4^{2-}$  ions. The experiments were performed with melamine tablets (PFEL-15; 5 x 17 mm; 1.13 ml vol.), in 20-25 ml cells with a flow rate of 100-150 ml/min. Evaluation of the adsorption isotherms demonstrated that in the case of HSA the rate of external diffusion is the limiting factor in adsorption, with the effective diffusion coefficient an order of magnitude greater than in solution ( $6.1 \times 10^{-7} \text{ m}^2 \text{ sec}^{-1}$ ). In the case of  $\text{MoO}_4^{2-}$  the effective diffusion coefficient was calculated at  $3 \times 10^{-15} \text{ m}^2 \text{ sec}^{-1}$ , demonstrating that in this case internal diffusion is the limiting factor in ion adsorption. Figures 4; references 17: 14 Russian, 3 Western.

**Corrosion at Metal-Fireproofed Polyethylene Interfaces**

**927M0238D Moscow ZHURNAL PRIKLADNOY KHIMII** in Russian Vol 65 No 2, Feb 92 (manuscript received 09 Jan 91) pp 396-400

[Article by A.M. Dorfman, V.I. Mikhaylov, N.V. Semakina, V.I. Povstugar, L.L. Makarova, M.A. Pletnev, S.M. Reshetnikov and V.I. Kodolov, Izhevsk Mechanical Institute; Udmurt State University; UDC 620.193:678.742]

[Abstract] Polarization and mass spectrometry were utilized in assessing corrosion of St.30 steel samples coated with a 0.5 mm thick film of fireproofed high density polyethylene (3-32% by wt. polyvinylmethyl phosphonate). In the case of an undamaged film full corrosion protection was afforded under test conditions over a 56 day period of observation. However, film damage led to corrosion at the metal-polymer interface and was attributed to ingress of moisture following film breakdown. Decomposition of the coating was due to leaching of methylphosphonic acid. Consequently, use of fireproofed polyethylene should be limited to situations in which there is no threat of moisture gaining access to the metal-polymer interface. Figures 4; references 7: Russian.

**Synthesis of Water-Impermeable Methacrylic Acid (MAA)/MAA-Diethylammonium Copolymers For Use in Oil Recovery**

**927M0238E Moscow ZHURNAL PRIKLADNOY KHIMII** in Russian Vol 65 No 2, Feb 92 (manuscript received 14 Mar 91) pp 409-414

[Article by O.N. Kuznetsova and N.I. Avvakumova, Kazan Institute of Chemical Technology; UDC 678.744.33-13]

[Abstract] Two methods were evaluated for the synthesis of MAA/MAA-DEA (diethylammonium) copolymers since they suitable for use in oil recovery by providing a water-impermeable barrier for sequestration of water in oil wells. The results of kinetic studies, assessment of the degree of polymerization, and high-resolution  $\text{H}^1$  NMR studies on the products demonstrated that polymerization of MAA into polymethacrylic acid (PMA) and subsequent copolymerization of PMA with DEA was the more efficient approach. Copolymerization of MAA with DEA was marked by low yields and formation of  $\alpha$ -methyl- $\beta$ -diethylaminopropionic acid as a byproduct. Figures 3; tables 4; references 13: 11 Russian, 2 Western.

**A Method of Determining the Strength of Polymer-Filler Structures**

**937M0049B Alma-Ata IZVESTIYA AKADEMII NAUK KAZAKHSKOY SSR: SERIYA KHIMICHESKAYA** in Russian No 2, Mar-Apr 92 (manuscript received 24 Dec 90) pp 18-22

[Article by Sh.B. Battalova, Zh.Zh. Bayarstanova, Sh.Ye. Yerdenova, I.Ya. Sadchikov, and A.A. Likerova, Chemical Sciences Institute, Kazakhstan Academy of Sciences, Alma-Ata; UDC 541.183.2-678.046.3]

[Abstract] One way of determining the structural strength of polymer-filler structures is to study the behavior of model systems (i.e., suspensions of filler in diluted polymer solutions) on a Weiler-Rebinder instrument. Strength is determined on the basis of the tangential displacement of an Al-wafer submerged in the study suspension. The process was automated by not suspending the Al-wafer but instead bringing it into contact with one of the ends of a glass suspension and by securing the other end of the suspension to a strain gauge transducer connected to the automatic recording device of a potentiometer. The resultant static shear stress is automatically fixed on the tape of the automatic recorder and determined on the basis of a calibration curve that is in turn calculated by using a formula provided. The deviation of shear stress thus calculated from the average values of parallel measurements for various systems did not exceed 3%. The model system  $\text{CaCO}_3$  - surfactant - low-pressure polyethylene was studied. The studies performed established that modifying  $\text{CaCO}_3$ -shell limestone with anion-active materials, i.e., with stearic acid [ $\text{CH}_3(\text{CH}_2)_6\text{COOH}$ ] and stearox 6 [ $\text{C}_{17}\text{H}_{35}\text{COO}(\text{CH}_2\text{CH}_2\text{O})_6\text{H}$ ] increases the strength of polymer-filler structures. The technique of modification of the calcium carbonate by impregnation with surfactants from ethyl alcohol proved to be somewhat more effective than did impregnation with surfactants from either  $\text{H}_2\text{O}$  or  $\text{C}_6\text{H}_6$ . Infrared spectroscopy studies clarified the nature of the interaction of the modifier and filler. Specifically, the increase in structural strength that occurs when shell limestone is modified by stearic acid is the result of the chemical reaction of the functional groups of the anion-active surfactant with the filler. Stearox 6 appeared to be adsorbed on the shell limestone.

in accordance with the very same mechanism as stearic acid. Figures 2, tables 2; references 4 (Russian).

**The Pyrolysis and Combustion of Chlorine-Containing Polymers in the Presence of Aromatic Diamines**

93M0049C Alma-Ata *IZVESTIYA AKADEMII NAUK KAZAKHSKOY SSR: SERIYA KHIMICHESKAYA* in Russian No 2, Mar-Apr 92 (manuscript received 24 Jun 91) pp 27-32

[Article by A.Yu. Goncharov, T.B. Zhubanov, and K.M. Gibov, Chemical Sciences Institute, Kazakhstan Academy of Sciences, Alma-Ata; UDC 678.652.01:543.08]

[Abstract] The effect of selected aromatic diamines on the processes of pyrolysis and combustion of chlorine-containing polymers was studied. Specimens of commercial polyvinyl chloride, chloroprene rubber, chlorinated natural rubber, and chlorinated polyvinyl chloride were used along with the following aromatic diamines: 4,4-diaminodiphenylmethane; 4,4-diaminodiphenyloxide; 4,4-diaminodiphenylsulfide; benzidine; chloromphenylenediamine; and n-phenylenediamine. All of the aromatic diamines used were first purified by recrystallization from ethanol and by distillation at reduced pressure. A Derivatograph Q-1500 D was used to perform a thermogravimetric analysis of the study compounds in inert and oxidation atmospheres. A Specord-75 IR spectrophotometer was used for the infrared spectroscopy studies of the reaction products. The studies established that the decrease in the combustibility of the study polymers that occurs when diamines are added to them is due to the reaction of the fire-proofing compounds with the polymer matrix at elevated temperatures and to the formation of more heat resistant structures. Specifically, the diamines added to the chlorine-containing polymers catalyzed a dehydrochlorination process. The course of the secondary reactions underwent changes after the addition of the diamines as well. In an oxidizing medium at temperatures of 500 to 600°C there was a notable increase in the oxidation resistance of the structures formed. In an inert medium, the addition of the diamines resulted in the formation of branched and cross-linked structures and in the formation of a heat-resistance coke residue that reduced combustibility by reducing the yield of combustible destruction products. No such coke residue was formed in the absence of diamine. Figures 4, tables 3; references 6: 4 Russian, 2 Western.

**Producing Ecologically Pure Polymer-Based Microfertilizers From Industrial Wastes**

93M0051B Moscow *KHIMICHESKAYA PROMYSHLENNOST* in Russian No 2, Feb 92 pp 82-85

[Article by I.B. Rabinovich, Ye.A. Krylov, B.A. Yagodin, A.A. Sobachkin, V.A. Safonov; UDC 631.81.095.337]

[Abstract] A process was developed for producing a series of polymer-based (ion exchanger-based) copper-, zinc-, cobalt-, and manganese-containing microfertilizers from industrial wastes. Because synthetic ion exchangers were used as carriers for the new microfertilizers, the microfertilizers were rendered water-insoluble. This made it possible to make use of a fundamentally new mechanism for transferring microelements to soil, namely, by exchanging them with ions contained in the soil or else released by plants' roots. This eliminated the mineral losses that typically occur as a result of fertilizers being washed out of the soil. The new microfertilizers were produced by using a cationite synthesized from lignin-containing wastes of the paper and pulp industry (i.e., from sulfite liquors). Up to now, about half of the 3 million metric tons of such wastes generated each year in the former Soviet Union have been dumped into water reservoirs. The main stages in the new lignin recovery process are as follows: preliminary purification of the starting liquor to remove impurities (cellulose fibers, etc.); ion-exchange purification of the liquor to remove ammonium cations and metal impurities and produce free lignosulfonic acid; preliminary evaporation of the lignosulfonic acid; polycondensation of the acid followed by granulation of the polymer; rinsing of the polymer to remove the unreacted materials; and drying of the finished product to an equilibrium content of hydration water. The yield of finished product amounts to about 75% of the starting material. The new process also includes regeneration of the cation exchanger by an aqueous solution of SO<sub>2</sub> to produce ammonium bisulfate and cation exchanger suitable for repeated use. The resultant cation exchanger has an ion exchange capacity of  $1.9 \times 10^{-3}$  kg-Eq/kg with respect to SO<sub>3</sub>H,  $0.4 \times 10^{-3}$  kg-Eq/kg with respect to COOH, and  $2.4 \times 10^{-3}$  kg-Eq/kg with respect to OH (total capacity,  $4.7 \times 10^{-3}$  kg-Eq/kg). The cation exchanger has an osmotic stability of at least 90%. The microelements for the microfertilizers are obtained from industrial sewage containing the respective metals. The process for producing granulated microfertilizers based on recycled polymer combines the membrane and ion exchange methods and allows for the regeneration and repeated use of the water and a number of the components removed from the wastes. Agrochemical field and commercial tests of the newly developed microfertilizers in different soil and climate zones throughout the country have yielded positive results. It is estimated that using the microfertilizers produced by the new process will result in a cost savings averaging 30 to 50 rubles per hectare of crops depending on the type of crop (based on 1990 data). Figures 2, table 1; references 15: 9 Russian, 6 Western.

**Quantum Chemical Activity of Intermediates of the Anionic Polymerization of Styrene and Methyl Methacrylate**

937M0054A Ivanovo IZVESTIYA VYSSHIKH UCHEBNYKH ZAVEDENIY KHIMIYA I KHMICHESKAYA TEKHOLOGIYA in Russian Vol 35 No 1, Jan 92 (manuscript received 3 Aug 90) pp 90-95

[Article by A.F. Korunova, A.P. Karpinets, V.D. Bezuglyy, and S.V. Pushkarev, Physical Chemistry Department, Kharkov Polytechnic Institute; UDC 541.64]

[Abstract] A quantum chemical study of the reactivity of intermediates of the electrochemical polymerization of styrene and methyl methacrylate was conducted. The CNDO/2 method with standard parametrization was used to calculate the associates' geometric structure and electron structure. The change in  $\pi$ -electron energy in the different stages of the electrochemical polymerization process were estimated by the simple molecular orbitals method. Ionic associates including  $\text{Li}^+\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Ca}^{2+}$  were considered. Two types of associates were considered, i.e., planar types where the metal ions are on the molecule's axis of symmetry at the continuation of the C-O bond and nonplanar types where the cation is perpendicular to the plane of the radical over the O atom. The specific effect of the nature of the cation of the background electrolyte on the direction and speed of the individual stages of the process were interpreted. A total of eight specific reactions stages are discussed. The analysis showed that for ion pairs involving cations of alkaline metals except for a  $\text{K}^+$  ion, the nonplanar conformation has a lower total energy. In the case of  $\text{Ca}^{2+}$ , the planar conformation has the lower total energy. The negative energy of the highest occupied orbital was found to increase in the sequence  $\text{K}^+ < \text{Na}^+ \leq \text{Li}^+ < \text{Ca}^{2+}$  and was thus concluded to be a measure of associate strength. The O-M bond in the compounds examined was found not to be purely ionic but to instead manifest a significant amount of covalence. The spin density was largely localized on the oxygen atom. Tables 4; references 15: 10 Russian, 5 Western.

**The Use of Copolymers of Styrene and Sulfur in Rubber Mixtures Based on SKI-3**

937M0057A Moscow KAUCHUK I REZINA in Russian No 4, Apr 92 pp 6-8

[Article by A.V. Gonyukh, L.A. Averko-Antonovich, A.G. Liakumovich, and I.Yu. Averko-Antonovich; UDC 678.043:661.249.29]

[Abstract] A study was conducted to determine the feasibility of using sulfur-containing styrene oligomers as a vulcanizing agent for SKI-3 rubber. Copolymers of styrene with sulfur were produced by reacting styrene with a sulfur melt at temperatures of 136 to 140° C with several different reagent starting concentrations in accordance with the usual method. After the reaction had been conducted for 6 hours, a viscous dark brown

product formed with a 95-97% yield. A Brabender kneading machine was used to combine the rubber with the sulfur-containing styrene oligomers, and a Waters-150C gel chromatograph with refractometric and ultraviolet detectors was used to measure the molecular characteristics of the rubber and the copolymer. An R-100 rheometer (Monsanto) was used to study the vulcanization kinetics of the rubber mixtures. The studies performed confirmed the fundamental possibility of using sulfur-containing styrene oligomers to chemically modify SKI-3 rubber. At the temperatures normally used to produce rubber, the oligomers did not promote the mechanical destruction of SKI-3. They reduced the time to onset of prevulcanization somewhat; however, no reversion of curing was observed regardless of the dosing or different sulfur contents tested. The rheometric and physicomechanical characteristics of the vulcanized rubber resulting from the use of the oligomer vulcanizing agents were on a par with those produced by using elemental sulfur. Figures 2, tables 3; references 5 (Russian).

**A Study of Polymeric Materials Subjected to a Multifactorial Effect**

937M0058A Moscow KAUCHUK I REZINA in Russian No 3, Mar 92 pp 4-5

[Article by V.A. Baykov, V.N. Voloshin, R.G. Levit, and N.M. Maksimova; UDC 621.315.2.622]

[Abstract] The combined effects of high temperatures, high pressures, and the effects of petroleum products and aqueous-alkaline solutions on selected rubbers were studied. Rubbers based on ethylenepropylendiene rubber, butadiene-nitrile rubber, acrylate rubber, a copolymer of tetrafluoroethylene + hexafluoropropylene, a copolymer of tetrafluoroethylene + perfluoroalkylvinyl ether, a copolymer of tetrafluoroethylene + ethylene, and an experimental rubber based on a combination of ethylenepropylendiene rubber with 15% butadiene rubber with an elevated content of 1,2-links. The studies were conducted in a medium of diesel fuel and in aqueous-alkaline solutions with a pH of 10 or 12 at elevated temperatures (110, 130, 150, and 200° C). The butadiene-nitrile rubber was most resistant to the effects of diesel fuel; the polyester thermoplast also remained serviceable in diesel fuel at temperatures up to 130° C. It was recommended that polyester thermoplast be used as a sheathing material for cables intended for operation at temperatures up to 110° C and that butadiene-nitrile rubber be used for sheathings subjected to temperatures of up to 150° C. The experimental combination of ethylenepropylendiene rubber with 15% butadiene rubber proved to be most promising as a material for use in manufacturing insulation and cable sheathing. It was twice as resistant to petroleum products as ethylenepropylendiene rubber alone and, at the same time, manifested the best resistance to heat aging. Prototype cables manufactured from the new combination rubber withstood 10 cycles of high pressures at a temperature of 160° C in the fluids extracted

from oil wells, and prototype insulation manufactured from it passed tests in which they were kept under a constant voltage of 3 kV. Test batches of cables were developed from the new combination of ethylenepropylene diene rubber with 15% butadiene rubber and have been sent to oil fields in Western Siberia for field tests. Tables 5.

**A Mathematical Model of the Process of the Copolymerization of Butadiene With Divinylbenzene Under the Effect of a Modified Organosodium Initiator**

937M0058C Moscow KAUCHUK I REZINA in Russian No 3, Mar 92 pp 15-17

[Article by P.P. Shpakov, A.V. Zak, Yu.Ya. Svirkin, and Yu.B. Podolnyy; UDC 547.422.22-31:542.952.643:51.004.14]

[Abstract] A mathematical model was developed to describe the copolymerization of butadiene with divinylbenzene under the effect of an initiator consisting of a sodium- $\alpha$ -methylstyrene oligomer, 4,4-dimethyldioxane, and lithium isopropylate. The model's adequacy was checked by using experimental data that had not been used in solving the inverse chemical kinetics problem on which the model was based. The calculated values for the conversion of butadiene and divinylbenzene were consistent with the experimental data; however the experimental values obtained for the suspensions with double bonds were somewhat higher than the calculated values and did not go to zero over the course of time as the calculated values did. The incomplete transformation of the suspensions with double bonds and their lower level of activity under the conditions of the experiment in comparison with the calculated data were linked to an increase in the viscosity of the polymerization medium that in turn resulted in a decrease in the cross-linking constant that was not taken into consideration when the mathematical description was developed. The mathematical model developed was thus determined to be sufficiently adequate for use in controlling the synthesis of a polymer with specified molecular parameters as a function of initial conditions (process temperature, initiator and monomer concentrations, and organosodium compound:modifier ratio). Figure 1; references 5 (Russian).

**16th Annual Symposium on Polymer Destruction**

937M0058D Moscow KAUCHUK I REZINA in Russian No 3, Mar 92 pp 30-31

[Article by G.Ye. Zaikov; UDC 06.053:061.3:678.019.31]

[Abstract] The 16th annual symposium on polymer destruction was held from 4 to 6 September 1991 at Aston University in Birmingham England. The symposium was titled "Polymer Stabilization. Mechanism and Use" and was dedicated to world-renowned scientist Gerald Scott, who is a professor at Aston University. The

conference's sponsors included a number of leading firms with which Scott has been associated: British Petroleum, Ciba-Geigy, Ethyl Corporation, ACI, American Cyanamid, and Sumitomo Chemical. One hundred thirty scientists from 24 countries, including the USSR, the United States, Czechoslovakia, and Japan took part in the symposium. Ten plenary lectures and 10 concise reports were presented at the plenary sessions. Numerous podium reports were presented as well. Topics covered in the plenary reports included the following: reactions of nitroxyl radicals and their role in the photostabilization of polymers by restricted piperidines; the chemical and photochemical behavior of phenol antioxidants during the stabilization of polymers; stabilization of polyolefins during their  $\gamma$ -initiated destruction; self-decomposing polymers and environmental protection; chemical and physicochemical aspects of processes occurring in polyolefins when they are processed in melts; and thermooxidation destruction of polyether polyols. Synergism and antagonism in the action of stabilizers, the reaction of antioxidants with other stabilizers, the use of dithiocarbamates of a series of metals to stabilize polyolefins, and the simultaneous use of chemiluminescence and thermal analysis to study the vitrification temperature and oxidation stability of poly-N-vinyl-2-pyrrolidine were among the topics covered in the concise reports. Overall, the symposium reports demonstrated that the problem of the aging and stabilization of polymers remains critical from both theoretical and practical standpoints.

**Laws Governing the Formation of a Gas-Liquid Layer on Plates Made of Fabric Polymer Structures**

937M0061B Moscow KHMICHESKAYA PROMYSHLENNOST in Russian No 8, Aug 92 pp 485-489

[Article by A.V. Serov, L.Ya. Tereshchenko, and M.M. Borisenko; UDC 66.048.375:532.51]

[Abstract] The metal contact devices that are currently used in plate-type column mass exchangers are plagued by a number of problems, including high flow resistance (especially under elevated gas-phase loads), significant splash entrainment as a result of operation in a stream mode, and a relatively narrow range of operational stability). A new type of contact device has been proposed and tested that is largely free of these problems. It has been given the name "fiber contact device," and it is made of mesh screens (net) made from polymer synthetic threads by a weaving process. Specimen fiber contact devices made of synthetic monofilaments of polyethylene terephthalate (lavsan) and polytetrafluoroethylene (the fluoroplastic 2M) along with brass threads were subjected to tests to identify the laws governing liquid-gas layer formation on the new plate contact devices. As a result, the following mechanism of phase-contact surface formation was proposed. When liquid is present on a plate in the absence of bubbling and a specified static

hydrostatic gas head corresponding to the minimum value of  $\Delta P_{stat}$  (i.e., when the liquid is retained on the plate without any gaps), the shape and area of the surface represents a film deformed in the form of spherical segments resting on the plate contact device's mesh screen. A further increase in the gas pressure in the space under the mesh screen results in segments and in the formation of hemispheres at the site of the energy minima with respect to flow resistance. This corresponds to the maximum pressure difference on the plate contact device under conditions of a valve mode caused by the effect of surface stress forces ( $\Delta P_s$ ). The sites at which the hemispheres have formed serve as bubble formation centers, and their further growth is not limited by conditions of the feeding of gas from the space under the mesh screen. Instead, further growth of bubbles is linked

solely to the feeding of gas from under the adjacent spherical formations. The bubbles continue to grow to sizes corresponding to the conditions of separation and surfacing. The phase-contact surface of plate contact devices is thus dictated by the surface of the bubbles formed in accordance with the mechanism discovered and by the surface of the film pulsing on the mesh screen. The frequency of the pulsations is proportional to the bubble formation frequency and, consequently, to the plate contact device's gas-phase productivity. This mechanism was confirmed by laboratory, bench, and industrial tests at a number of enterprises throughout the chemical industry. These tests also established that the new polymer mesh screens are capable of maintaining a constant flow resistance over a wide range of gas-phase loads. Figures 3, tables 2; references 6 (Russian).

**Effect of Structural Factor and Adsorbed Water on Radiolysis of Polysaccharides. 1 Communication. Radiation-Chemical Transformation of Macromolecules**

*937M0065A Moscow KHIMIYA VYSOKIKH ENERGIY in Russian Vol 25 No 5, Sep-Oct 92 (manuscript received 15 Feb 89, after final revision 27 Jan 92) pp 423-428*

[Article by G. A. Fedorova, N. T. Bondarenko, S. M. Berlin, S. V. Volkovich, V. A. Sharpatyy, Institute of Physical-Organic Chemistry, Academy of Sciences of Belarus; Institute of Chemical Physics imeni N. N. Semenov, Russian Academy of Sciences; UDC 541.15 + 538.113 + 539.199]

[Abstract] Effective management of  $\gamma$ -radiolysis during processing and modification of crude vegetable material depends on the knowledge of the reaction mechanisms involved. Effect of the structural factor on radiation-chemical destruction and modification of native

polysaccharides was investigated in a wide range of adsorbed doses. The study was done on potato and amylopectine starch, on cotton cellulose and of lyophilized dextran. The destruction and modification of all polysaccharides is based on the same competing processes of the conversion of primary macroradicals (hydrolysis of macroradicals, their isomerization with bond breakage,  $\alpha$ - or  $\beta$ -elimination of water, formation of ROO-type radicals in presence of  $O_2$ , etc). First of all, the amorphous areas of the polymers are broken down. The yield and composition of the final products is determined by the presence of water molecules close to the macroradical and obviously by the accessibility of H or OH radicals to a carbon atom for a direct interaction. Depending on the specific structure, one of the processes occurs in each of the polysaccharides during the irradiation : a break of the H bonds, "clean" destruction, or radiation-chemical modification. Table 12; figure 1; references 18: 10 Russian, 8 Western (2 by Russian authors).

**Impact of Flow Rate on Response Times of Br<sup>-</sup> and I<sup>-</sup> Selective Electrodes**

*927M0238F Moscow ZHURNAL PRIKLADNOY KHIMII in Russian Vol 65 No 2, Feb 92 (manuscript received 30 Jul 91) pp 426-428*

[Article by A.N. Khutishvili, E.I. Bondarenko and Yu.Ye. Yermolenko, Analitpribor Scientific Industrial Association; UDC 541.135:543.257.1]

[Abstract] Concentration jumps and flow rate variations were used to investigate response times of ion selective electrodes with AgBr-Ag<sub>2</sub>S and AgI-Ag<sub>2</sub>S crystalline membranes. The results demonstrated that the response time was inversely related to the concentration over a potential range of 0 to ca. 50+ mV. The graphical data showed that the response time reached a minimum value and plateaued at flow rates of ca. 8 m sec<sup>-1</sup>. These observations indicated that—under those conditions—the diffusion sublayer at the electrode surface was not further affected by membrane irregularities, ion mobility or potential-dependent electrochemical reactions. Figures 3; references 5: 1 Russian, 4 Western.

**Dissolution of Silver in the System DMSO-HBr**

*937M0063D Moscow IZVESTIYA AKADEMII NAUK RAN: SERIYA KIIIMICHESKAYA in Russian No 8, Aug 92 (manuscript received 13 Feb 92) pp 1929-1930*

[Article by L.V. Shirshova and L.P. Lavrentyev, Structural Macrokinetics Institute, Russian Academy of Sciences, Chernogolovka; UDC 541.127:542.943:546.141:546.557]

[Abstract] Previous studies of the oxidative dissolution of silver in the donor-acceptor electrotransport system

dimethyl sulfoxide [DMSO]-HBr established that the dissolution process reaches its maximum at an HBr concentration of 83 mol.-%. Further studies of the oxidative dissolution of silver in DMSO-HBr donor-acceptor systems with HBr concentrations of less than 4 mol.-% (specifically, 3.5, 3.0, 2.2, and 1.5 mol.-%) have established that the silver dissolution process actually has two maxima. The first occurs at an HBr concentration of 3 mol.-%, and the second occurs at an HBr concentration of 83 mol.-% (as reported previously). The dissolution process rate at the point of the second maximum is 3.7 times greater than at the point of the first maximum. Figure 1; references 2 (Russian).

**Study of Gold Complex Formation With 4-Methylphenylazorhodanine**

*937M0064A Moscow KOORDINATSIONNAYA KHIMIYA in Russian Vol 18 No 9, Sep 92 (manuscript received 4 Mar 91) pp 992-995*

[Article by O. V. Mandzhaladze, N. N. Basargin, N. M. Teliya, D. G. Chichua, Tbilisi State University imeni I. Dzhavakhishvilli; UDC 541.49.543.062]

[Abstract] Complex formation between gold and 4-methylphenylazorhodanine was investigated using a 10-fold excess of the reagent. The reaction is rapid, reaching a maximum color development in about 15 minutes. Because the outcome depended on the order in which the reagents were mixed, the gold solution was introduced first into the reaction vessel, followed by a solution of the reagent and finally by the buffer solution or the acid. The 1:1 complex obtained is stable in solution for about 2 hrs. Based on spectrophotometric data, the complex consists of two components: an anionic complex AuCl<sub>4</sub><sup>-</sup> and an external sphere cation 4-methylphenylazorhodanine-H<sup>+</sup>. Figures 2; references 20: 12 Russian (3 by Western authors), 8 Western.

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